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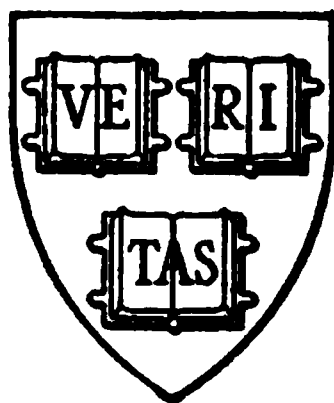
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THE JOURNAL  
—OF THE—  
AMERICAN CHEMICAL SOCIETY.

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VOLUME XX.

1898.

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COMMITTEE ON PAPERS AND PUBLICATIONS:

EDWARD HART, Editor,

J. H. LONG,

EDGAR F. SMITH.

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# THE JOURNAL

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### A NEW FORM OF DISCHARGER FOR SPARK SPECTRA OF SOLUTIONS.

BY L. M. DENNIS.

Received November 10, 1897.

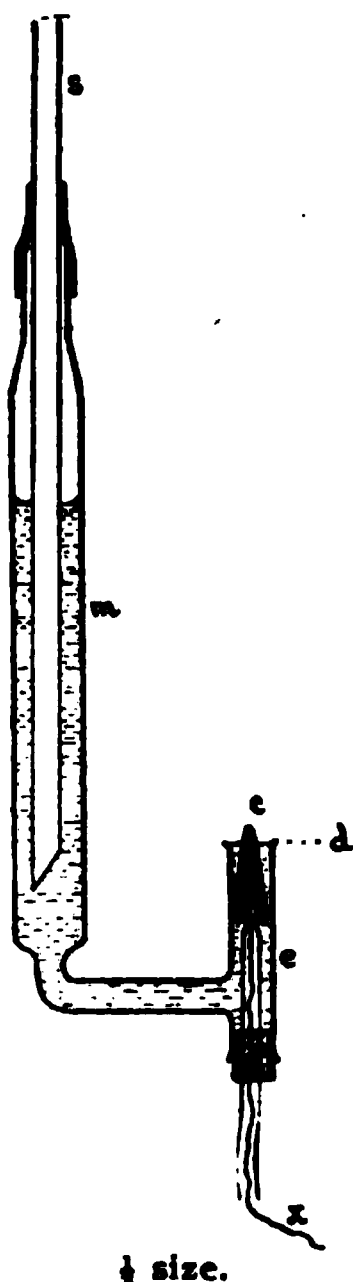
**M**ANY forms of dischargers for examining the spark spectra of solutions have been described, but all of those with which the writer is acquainted possess disadvantages that seriously impair their value.

To prevent the spattering of the liquid upon the slit of the spectroscope the terminals are, in some cases, surrounded by a glass tube. If a spark of even moderate intensity be used, the liquid which is thrown against the walls of the tube soon cuts off most of the light and obscures the spectrum. It is then necessary to disconnect the discharger and to thoroughly clean the walls of the tube, an operation wasteful both of time and material. Others recommend that the glass tube be abandoned and that free terminals be employed. In this case it becomes necessary to place the spectroscope at some distance from the discharger to avoid the spattering of the liquid against the slit. Again, if the observations are at all prolonged, the liquid in the discharger is soon used up to such an extent that the lower terminal becomes too dry to give a brilliant spectrum. The discharger must then be refilled.

These difficulties are obviated by the following device which we have been using for the past year. No striking originality

is claimed for it, and the chief excuse for here describing it is furnished by its usefulness.

The lower terminal consists of a platinum wire  $x$  and the graphite cone  $c$ . The cone is bored as shown to permit of its



being slipped over the end of the platinum wire, and the upper end of the cone is allowed to project slightly above the end  $d$  of the glass tube  $e$ . The platinum wire passes through a small glass tube, the upper end of which is fused together about the wire. This tube is held in place by a small cork. The remainder of the apparatus is made of glass tubing of the form as shown. The upper end of  $m$  is drawn out so that there may be slipped over it a piece of rubber tubing small enough to hold the tube  $s$ . To fill the apparatus, the tube  $s$  is removed, the discharger is inclined to the left, and the liquid is run in at the upper end of  $m$ .  $s$  is then inserted and pushed down nearly to the bottom of  $m$ . Upon now bringing the apparatus into the upright position, the liquid in the side arm  $e$  will rise until on a level with the lower end of  $s$ .  $s$  is then carefully drawn up until the liquid in  $e$  has risen to the point  $d$ . As the liquid is evaporated

by the spark at the terminal  $c$ , it will be maintained at the level  $d$  by the entrance of air through the lower end of  $s$ , and this will continue until the liquid in  $m$  has fallen until about on a level with  $d$ .

The employment of terminals made from Ceylon graphite was first suggested by Hartley,<sup>1</sup> who used pieces shaped like a wedge and made contact between the platinum wire and the carbon cone by wrapping the wire around the cone. The form here suggested permits of an easy removal of the terminal and its replacement by an electrode of other material. If a platinum terminal is desired, the carbon cone is removed and the glass tube carrying the platinum wire is pushed up until in the proper position.

<sup>1</sup>Trans. Royal Society. 175. 52.



The form of discharger above described leaves the terminals free and exposes the slit to spattering. This difficulty is removed by simply covering the slit with a glass microscope slip of suitable size. We use a slip three inches long by two wide and about one-sixteenth of an inch in thickness, and hold it in place by two rubber bands. If the glass becomes spattered, it can easily be wiped clean or replaced by a clean slip.

The upper terminal, which is not shown in the figure, consists of an insulated platinum wire or a graphite cone, around which the wire is wrapped.

CORNELL UNIVERSITY,  
October, 1897.

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## VINEGAR ANALYSIS AND SOME CHARACTERISTICS OF PURE CIDER VINEGAR.

BY ALBERT W. SMITH.

Received November 17, 1897.

THE laws of Ohio, copying the food laws of several older states, require, among other things, that apple or cider vinegar to be sold in the state shall contain at least two per cent. of cider vinegar solids. As to the chemical composition of what constitute the solids of pure cider vinegar, very little has been published. The *Analyst* for May, 1891, contains some analyses of pure malt vinegar and the prosecution, in 1893, of several cases in the courts of England, by the food inspectors against dealers in distilled and wood-acid vinegar, attracted considerable attention in that country to the subject of the chemical composition of vinegar and methods of distinguishing from each other the several kinds of vinegar upon the English market. Some valuable data were published by Allen and Moore,<sup>1</sup> especially concerning the character of vinegar made from grain. From the discussion of the question by the Society of Public Analysts<sup>2</sup> it appears that the English vinegar market is largely supplied by products made from distilled alcohol and from malted or unmalted grain. In this country the principal sources of vinegar are from apple cider and from distilled alcohol, the

<sup>1</sup> *Analyst*, 18, 240; and 19, 214.

<sup>2</sup> *Analyst*, 18, 180 and 240, 19, 8 and 33.

latter being usually made from maize and malt. Almost all of this distilled or spirit vinegar, which is originally nearly colorless, is colored by caramel in imitation of the color of cider and malt vinegar.

The chemical distinction between cider and spirit vinegar, when pure, offers little difficulty. The cider vinegar, except that made from early summer apples, is of a dark brown color, contains from two and a half to four per cent. solids and 0.30 to 0.50 per cent. ash, and when old has a pleasant, fragrant odor and characteristic taste. The distilled vinegar contains little solid matter and almost no ash, with little taste or odor besides that imparted by its acetic acid contents. The caramel used in this coloring is usually made by burning or caramelizing glucose or from an aqueous extract of charred grain. Although many manufacturers stoutly contend its use to be to impart flavor and "body" to the vinegar, the palpable and sole object of the coloring process is to enable the unscrupulous dealer to sell the product for "pure cider vinegar" or "pure malt vinegar," which, to my personal knowledge, was the all too common practice in Ohio until the statutes against food adulteration were vigorously and honestly enforced.

The chemical distinction of the source of a sample of vinegar must depend largely upon the quantity and composition of its solid constituents. The organic portion of these solids would seem to offer an excellent opportunity for differentiation, in its maleic and succinic acids, glycerol and sugar contents, and the accurate determination of these would undoubtedly furnish the most valuable basis for judgment. At present, however, the methods in use for the determination of each of these are so tedious and, in the end, so unsatisfactory, that the mineral contents of the ash afford a more advantageous and practical method for the public analyst.

The ash of cider vinegar differs from that of most other kinds in a number of characteristics, only a few of which have heretofore been pointed out.<sup>1</sup>

The first peculiarity to be noticed is that the ash from cider vinegar commences to volatilize and is fusible at a comparatively

<sup>1</sup> Allen : Commercial Organic Analysis, 1, 389; Cox : *Analyst*, 19, 89.

low temperature. If the ash fuses before all the carbon is burned, particles of this are apt to become enclosed and then to resist further oxidation. To prevent this it is best to evaporate and burn small quantities at a time (not to exceed ten cc.), and to keep the temperature as low as is consistent with complete oxidation. A low red heat must not be exceeded, else loss by volatilization occurs.

A second qualitative difference is the fact that the ash from pure cider furnishes a potassium flame unobscured by sodium light, which is usually not the case with a vinegar containing much added natural water, as imitations usually do.

The ash of cider vinegar differs quantitatively from others so far examined in being quite low in chlorides and sulphates, and high in alkaline carbonates and phosphates. A determination of each of these is quickly and easily made by volumetric methods and the results afford data from which reliable conclusions as to the genuineness of the sample may be drawn. About two-thirds of the phosphates of pure cider vinegar ash are soluble in water. In the ash of other vinegars upon the market a much lower proportion of the total phosphates is soluble in water, and the addition of natural water containing lime or magnesia, to pure cider vinegar, reduces this proportion of soluble phosphates, by converting potassium into alkaline earth phosphates.

The complete analysis may be conveniently carried out as follows: For solids, five to ten grams are evaporated in a flat-bottomed dish and dried to constant weight in a water oven. For total acidity five grams, diluted to about fifty cc., are titrated with standard alkali, using phenol-phthalein as indicator. The result is usually reported as acetic acid, without attempting to separate this from the small amounts of other organic acids present.

For ash, ten grams are dried and burned in a crucible, using the before-mentioned precaution of a low temperature. This is weighed and dissolved, and the solution tested qualitatively for color of flame and presence of sulphates and chloride. Unless these are excessive, as compared with a sample of known purity, they need not be determined quantitatively.

For alkalinity of ash and proportion of phosphates, twenty-five

grams are dried and burned, the ash extracted repeatedly with hot water, and the aqueous solution titrated with standard acid, using methyl orange as indicator. The undissolved residue of ash is then treated with nitric acid, the solution partially neutralized, and the phosphorus in each solution separately precipitated by molybdate solution, the yellow precipitate dissolved in ammonia, reduced with zinc and sulphuric acid, and titrated with standard permanganate solution.

All colored samples should be tested for coloring-matter, which, in imitation vinegars, is most commonly caramel. To test for this, mix five to ten cc. of the sample with about twenty-five cc. paraldehyde, and add alcohol until the three liquids become soluble. After standing twelve to twenty-four hours, the caramel will separate as a sticky, dark-brown precipitate, which, after washing with a little absolute alcohol, has the characteristic bitter taste of caramel, and reduces Fehling's solution freely.

#### TWENTY-TWO SAMPLES PURE CIDER VINEGAR.

Number.	Acetic acid.	Total solids.	Ash.	No. cc. tenth-normal acid required to neutralize ash from 100 grams vinegar.	Millig'ns $P_2O_5$ in water solution of ash from 100 gms.	Millig'ns $P_2O_5$ in ash not soluble in water.	Total $P_2O_5$ in ash from 100 grams vinegar.	Original solids = Solids + $\frac{1}{14} \times$ acetic acid.	Ash per 100 parts original solids.	$P_2O_5$ millig'ns per 100 grams original solids.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1	5.46	2.27	0.44	43.9	22.7 <sup>1</sup>	16.3	39.0 <sup>1</sup>	10.46	4.21	373
2	3.29	2.69	0.36	31.2	17.3	8.7	26.0	7.63 <sup>2</sup>	4.72	341
3	4.22	3.21	0.36	36.0	18.5	9.2	27.7	9.54	3.77	290
4	3.58	2.91	0.31 <sup>2</sup>	28.4 <sup>2</sup>	15.6	4.2 <sup>2</sup>	19.8 <sup>2</sup>	8.28	3.74	239
5	3.74	2.14	0.31	36.0	17.5	7.8	25.3	7.75	4.00	326
6	4.74	2.80	0.35	34.4	18.3	6.8	25.1	9.91	3.53	253
7	4.59	2.86	0.32	32.8	19.5	13.8	33.3	11.74	2.73 <sup>2</sup>	284
8	4.19	3.00	0.33	36.8	20.5	8.5	29.0	9.28	3.55	312
9	4.92	4.45 <sup>1</sup>	0.38	30.8	17.8	9.5	27.3	11.83	3.21	231
10	4.63	3.30	0.40	47.2	21.3	9.8	31.1	10.24	3.90	303
11	3.24 <sup>2</sup>	3.89	0.44	45.2	20.5	10.8	31.3	8.78	5.01	348
12	3.89	3.00	0.33	30.4	22.5	10.5	33.0	8.88	3.72	372
13	4.97	2.40	0.37	44.0	15.5	11.0	26.5	9.85	3.76	269
14	6.55	2.76	0.49	44.8	17.0	4.6	21.6	12.58	3.89	172 <sup>2</sup>
15	4.11	2.43	0.36	28.8	21.2	5.6	26.8	8.60	4.19	312
16	7.61 <sup>1</sup>	2.97	0.43	55.2 <sup>1</sup>	21.0	11.0	32.0	14.38 <sup>1</sup>	2.99	223
17	4.00	2.53	0.34	35.2	19.4	11.3	30.7	8.53	3.98	360
18	4.08	2.82	0.33	36.0	13.6 <sup>2</sup>	19.4 <sup>1</sup>	33.0	8.94	3.69	369
19	4.00	2.75	0.51 <sup>1</sup>	45.6	17.5	15.5	33.0	8.75	5.83	377 <sup>1</sup>
20	3.80	2.50	0.50	48.8	19.9	9.0	28.0	8.20	6.09 <sup>1</sup>	352
21	4.20	2.00 <sup>2</sup>	0.39	44.0	19.9	9.0	28.9	8.29	4.70	348
22	4.30	2.50	0.46	40.0	22.5	10.0	22.5	8.95	5.14	365
Aver.	4.46	2.83	0.39	38.8	19.1	10.1	28.6	9.65	4.11	310

<sup>1</sup> Maximum.

<sup>2</sup> Minimum.

**TWENTY-SEVEN SAMPLES CIDER VINEGAR CONTAINING ADDED WATER OR  
ADDED SPIRIT VINEGAR SOLD IN OHIO MARKETS.**

Number.	Acetic acid. (1)	Total solids. (2)	Ash. (3)	No. cc. tenth-normal acid required to neu- tralize ash from 100 grams vinegar. (4)	Millig'ms $P_2O_5$ in water solution of ash from 100 gms. (5)	Millig'ms $P_2O_5$ in ash not solu- ble in water. (6)	Total $P_2O_5$ in ash from 100 gms. vinegar. (7)	Original solids $= \text{Solids} + \frac{1}{14} \times$ acetic acid. (8)	Ash per 100 parts original solids. (9)	$P_2O_5$ millig'ms per 100 grams original solids. (10)
1	4.10	2.64	0.53	24.4	none	8.4	8.4	8.79	6.03	95
2	4.21	2.94	0.47	10.8	15.2	8.1	23.3	9.25	5.08	252
3	4.11	2.50	0.28	24.4	4.4	4.0	8.4	8.66	3.23	97
4	3.84	2.35	0.30	9.8	4.4	20.2	24.6	8.11	3.70	303
5	4.31	2.10	0.27	24.0	12.8	8.5	21.3	8.56	3.15	249
6	4.26	2.41	0.27	26.8	15.0	5.0	20.0	8.80	3.07	227
7	4.15	2.35	0.27	29.6	...	...	...	8.58	3.15	...
8	4.07	2.14	0.27	27.6	...	...	...	8.24	3.27	...
9	4.01	2.09	0.26	23.0	12.0	5.0	17.0	8.10	3.21	210
10	3.84	2.06	0.26	26.4	...	...	...	7.82	3.33	...
11	3.43	1.69	0.25	18.8	12.0	12.0	24.0	6.83	3.66	351
12	4.46	2.99	0.25	16.6	6.0	3.0	9.0	9.68	2.58	94
13	3.73	1.21	0.25	1.4	none	7.5	7.5	6.81	3.67	110
14	3.97	1.91	0.24	22.8	5.3	8.8	14.1	6.86	3.50	205
15	4.83	2.20	0.24	21.6	11.4	15.8	27.2	9.44	2.54	288
16	3.68	2.45	0.23	15.6	8.6	6.6	15.2	7.97	2.88	191
17	4.00	1.74	0.22	25.2	5.8	8.4	14.2	7.74	2.84	183
18	3.65	1.42	0.20	17.6	...	...	...	6.89	2.90	...
19	4.70	2.14	0.20	13.4	10.0	10.5	20.5	9.19	2.18	223
20	3.01	3.41	0.20	20.8	...	...	...	7.92	2.53	...
21	3.84	1.90	0.20	27.6	5.2	15.2	20.4	7.66	2.61	266
22	4.10	1.20	0.18	14.4	5.0	3.0	8.0	7.35	2.45	109
23	3.88	1.57	0.18	13.0	...	...	...	7.39	2.43	...
24	3.74	1.41	0.17	9.6	...	...	...	7.02	2.42	...
25	4.62	2.02	0.17	11.2	5.8	3.0	8.0	8.95	1.90	89
26	3.44	1.19	0.14	14.0	...	...	...	6.35	2.20	...
27	4.03	1.64	0.14	7.4	trace	4.5	4.5	7.68	1.83	59

**SAMPLE MADE FROM DRIED APPLES AND GLUCOSE.**

4.29	3.89	0.25	21.0	..	..	5.5	10.33	2.42	53
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**SAMPLE MADE FROM APPLE CIDER AND GRAPE JUICE.**

4.54	2.77	0.30	34.0	..	..	4.0	9.58	3.13	42
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**FOUR SAMPLES MALT VINEGAR.**

Eng.	5.90	2.21	0.28	6.0	..	..	12.5	11.06	2.53	113
Am.	5.16	2.67	0.26	6.0	..	..	9.0	10.41	2.50	86
"	4.40	2.04	0.23	5.6	..	..	9.2	8.64	2.66	106
"	4.01	1.75	0.20	4.4	..	..	9.5	7.76	2.58	122

**SIXTY-FIVE SAMPLES SPIRIT VINEGAR.**

Av..	3.84	0.38	0.06	1.1	none	trace				
Max.	5.99	0.78	0.15	5.6	"	"				
Min.	2.87	0.14	0.01	0.0	"	"				

In columns 1, 3, 5, and 8 of the accompanying tables, results are stated as grams per 100 grams of the sample. In column 4 are given the number of cubic centimeters of decinormal acid required to neutralize the filtered water solution of the ash derived from 100 grams of the vinegar. In columns 5 and 6 are the number of milligrams of phosphorus pentoxide ( $P_2O_5$ ) respectively in the water solution and the water insoluble portion of the ash derived from 100 grams of the sample. Column 7 contains the sum of these two quantities, or the total phosphorus pentoxide. In column 8, what Hehner<sup>1</sup> calls "original solids" are given. These numbers are obtained by multiplying the acetic acid quantities by 1.5 and adding to this the total solids. It is assumed by Hehner that three parts of sugar by alcoholic and acetic fermentation yield two parts of acetic acid, this being approximately the theoretical quantitative relations:



Hence, by increasing the acetic acid in the ratio of two to three, we get approximately the theoretical quantity of sugar from which it was produced. By adding to this the amount of solids still remaining in the vinegar, the quantity of solids present in the unfermented liquid is assumed to be obtained. Of course such an assumption is extremely far from the truth, because, from various losses during fermentation, by volatilization of alcohol and acetic acid, only one-half to three-quarters of the theoretical yield of acid is obtained, and this loss varies greatly in the different processes, and in the same process depends largely upon individual care during each of its steps. Further, during the fermenting and settling periods albuminoid and other constituents settle in considerable quantities, so that such calculations possess little real worth, and, when spirit vinegar is used as an adulterant of cider or malt vinegar, they may become decidedly misleading. The figures in columns 8, 9, and 10 are given principally for the sake of comparison with previous analyses which have been reported in this way. In column 9 the percentages of ash to "original solids," found in column 8, have been given, obtained by dividing 100 times the

<sup>1</sup> *Analyst*, 16, 82.

per cent. of ash as given in column 3 by the per cent. of "original solids." In the same way the milligrams of total phosphorus pentoxide per 100 grams of original solids are reported in column 10.

Of these results, the quantity of ash, the alkalinity of the ash, and amount of soluble phosphates are of considerable uniformity in pure cider vinegar, and these, when considered with the other characteristics above enumerated, serve to differentiate this kind quite sharply from all other commercial varieties and to afford a basis for the approximate estimation of the quantity of spirit vinegar or of water, with which pure cider vinegar may have been adulterated.

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[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY,  
OHIO STATE UNIVERSITY.]

## ROOT TUBERCLES IN WATER CULTURE.<sup>1</sup>

BY H. A. WEBER.

Received November 22, 1897.

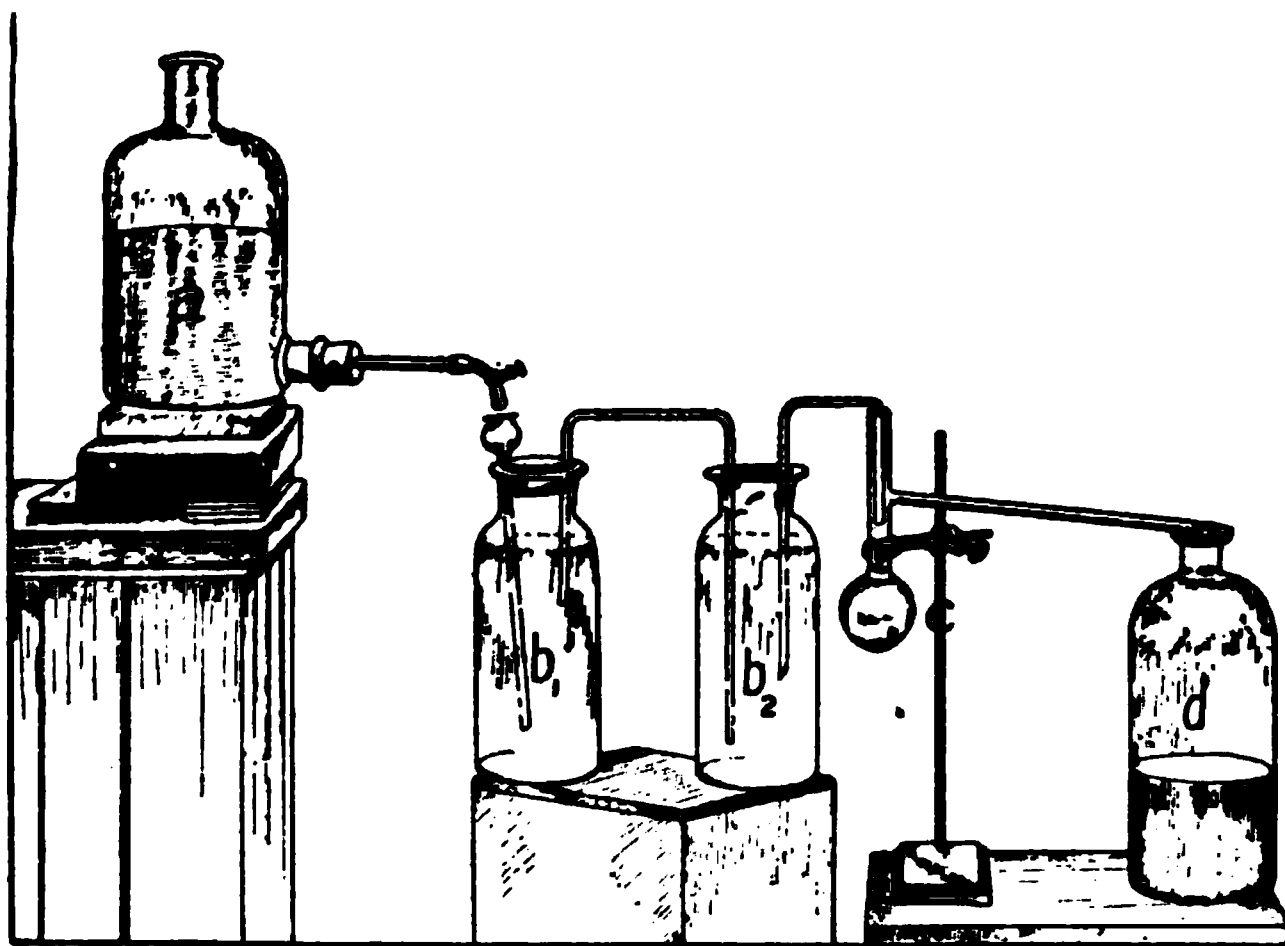
SINCE the discovery by Hellriegel of the connection between root tubercles and the fixation of atmospheric nitrogen by leguminous plants, the literature on this interesting and important question is being constantly enriched by painstaking experiments on the part of scientific investigators all over the world. The subject has thus far been studied only in connection with sterilized soil or sand. It occurred to the writer that it might be possible to produce root tubercles in water culture and thus be able to observe the process better than when the roots of the plants were buried in soil or sand. The work of conducting the experiments about to be described was entrusted to Mr. J. C. Britton, one of the writer's advanced students. The results more than met my expectations, and this preliminary notice is made public for the benefit of those who may feel inclined to employ the method in their investigations.

For the past four or five years the writer has employed in water-culture experiments an apparatus designed by himself, which presents certain advantages over the methods heretofore described. As this apparatus was employed in the experiments

<sup>1</sup> Read before the Columbus Section of the American Chemical Society, Nov. 10, 1897.

under consideration, a brief description of the same may not be out of place.

As will be seen from the accompanying illustration, *a* is an aspirator of four liters capacity; *b*<sub>1</sub> and *b*<sub>2</sub> are ordinary salt mouth bottles of two liters capacity, which serve as culture jars; *c* is a small flask with a side tube, as used in fractional distilla-



tion; *d* is a collecting bottle of four liters capacity. The culture jars are fitted with cork disks to hold the plants in the usual manner and also support the thistle tube and the siphons as shown in the illustration.

At the beginning of a vegetation experiment, the flask *c*, the culture jars, and the aspirator, are filled with the nutrient solution. The aspirator is closed with a rubber stopper carrying a glass tube, to the end of which a short piece of rubber tubing is attached. In this manner the solution is conveyed to the thistle tube, which extends to near the bottom of jar *b*<sub>1</sub>, the flow being controlled by means of a Hoffman clamp placed on the rubber tubing. By means of a siphon, the short arm of which extends a short distance below the surface of the solution in jar *b*<sub>1</sub>, and the long arm nearly to the bottom of jar *b*<sub>2</sub>, the solution flows into jar *b*<sub>2</sub>.

Another siphon with one arm extending a short distance



below the surface of the solution in jar *b*, and the other below the side tube in flask *c*, carries the solution into flask *c*, from which it runs through the side tube into the collecting bottle. The drop of the solution into the thistle tube is so regulated that the aspirator will empty itself in about twenty-four hours, when the solution in the collecting bottle is transferred back into the aspirator. This is done once a day until the vegetation experiment is completed.

The advantages of this arrangement are :

1. Two seedlings, or if, as the writer has frequently done, another culture jar be inserted between jar *b*, and the flask *c*, three seedlings can be grown in the same solution at the same time, so that, if an accident should happen to one of the seedlings, the experiment need not necessarily fail.

2. The solution is continually being aerated as it drops into the thistle tube and into the collecting bottle, as well as when it is transferred to the aspirator. By this means the roots of the seedlings are constantly supplied with free oxygen, a condition necessary for healthy growth.

3. Plants can be grown to maturity without removing them to other jars filled with fresh solutions.

4. The solution in the culture jars always remains at the same level, *i. e.*, on a level with the side tube of the flask.

Two solutions were prepared as follows :

1. COMPLETE NUTRIENT SOLUTION (Wolff's Solution).

	Grams.
Bone ash dissolved in nitric acid.....	20
Potassium nitrate.....	11
Magnesium sulphate.....	7
Potassium chloride.....	3
Ferrous sulphate.....	Minute quantity

The whole dissolved in distilled water, neutralized with sodium carbonate, and diluted to one liter.

2. COMPLETE NUTRIENT SOLUTION WITHOUT NITROGEN.

	Grams.
Bone ash dissolved in nine cc. sulphuric acid.....	20.0
Potassium sulphate.....	9.5
Magnesium sulphate .....	7.0
Potassium chloride.....	3.0
Ferrous sulphate.....	Minute quantity

The whole dissolved in distilled water, neutralized with sodium carbonate, and diluted to one liter. For the growing of plants

the apparatus was filled with a mixture of the respective solutions and distilled water in the proportion of five cc. of the solutions to one liter of water. Trials with fifteen cc., and even ten cc. of the solutions to one liter of water, failed on account of over-nutrition, the seedlings refusing to grow and finally dying.

The plants employed were dwarf peas. The seeds were made to germinate in sterilized sand, moistened with distilled water. When the seedlings were four or five inches in height, they were taken from the sand, the roots washed and the plants transferred to the culture jars.

Three sets of apparatus, as shown in the illustration, were provided. The first set contained the complete nutrient solution. The second set contained solution No. 2, as described above, without nitrogen.

The third set contained the same solution, but in addition the seedlings before being placed into the jars, were inoculated with tubercle germs, by immersing the roots for a few minutes in a cold water infusion of a soil, in which peas had been grown.

As might be expected, the plants in set No. 1, containing the complete nutrient solution, were healthy and vigorous, and produced flowers and fruit.

The plants in set No. 2 grew rapidly for a time, but were weak and sickly in appearance. In about ten days the leaves began to turn yellow and to show the effect of nitrogen starvation. A few small blossoms finally appeared, but this caused the speedy death of the plants. The roots developed very rapidly, completely filling the jars. They were doubtless in search of nitrogenous food.

The plants in set No. 3 grew normally for about ten days, when they began to show the effect of nitrogen starvation in a marked degree. No tubercles could be observed on the roots. About the thirteenth day the plants began to recuperate, the leaves assumed a normal green color, and from this time on the growth was vigorous and normal. On the fifteenth day the tubercles were first observed, but they had then attained considerable size.

The plants, like those of set No. 1, produced flowers and fruit. Investigations in this direction will be continued.

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## DERIVATIVES OF SILICON TETRACHLORIDE.<sup>1</sup>

BY JOSEPH F. X. HAROLD.

Received December 1, 1897.

### GENERAL REMARKS UPON COMPOUNDS OF THE HIGHER HALOIDS OF THE ELEMENTS OF GROUP IV.

THE review of the reactions of these tetrachlorides furnishes some interesting data from which inferences of importance may be drawn. There are, however, numerous problems still unsolved, and many reactions that yet demand study, before any broad comparison of the behaviors of these elements can be definitely made, or any conclusion as to the influence of the atomic weight or metallic character on the reactivity of their tetrachlorides established. No general rule could be deduced from the data already collected, which would enable us by a logically drawn analogy, to predict their behaviors in certain uninvestigated reactions.

Carbon and silicon, the first two elements of the group, are by their position more or less isolated, and removed from too close a comparison with any of the sub-group elements, and their reactions are best studied with a view to determining or increasing their own already well developed similarities, without seeking to broaden to too great an extent their relation to other elements of the group. The chlorides of silicon and carbon may be said, however, in a general way, to possess in common with the other group members, a distinctly acid nature, and to exhibit the power of combining with bases to form stable, well defined compounds. This behavior may be predicted for even the unstudied chlorides of germanium, lead and thorium, since every element thus far investigated has in its tetrachloride form thus deported itself. Ammonia, the substituted ammonia derivatives, such as methylamine, toluidine, urea and amido bodies of a distinctly basic character, may here be said to react similarly with all. With acid amides and bodies of a distinctly acid nature, no such general rule may be adopted, and a series of reactions occur which seem to be conditioned by no rise or fall in atomic weight

<sup>1</sup> Thesis presented to the University of Pennsylvania for the degree of Doctor of Philosophy.

or by position and group relation of the elements. Titanium, one of the elements of the sub-group having a less metallic character, and tin of the opposite sub-group and of a distinctly metallic nature and a high atomic weight, represent the most reactive of the elements of Group IV, in their tetrachloride form. Other than this, there seems to be little relationship between them, being distinctly separated by such considerations as place them in opposite groups. Titanium, the element of lowest atomic weight of the first sub-group, is in its quadrivalent form most reactive. Its tetrahaloid forms derivatives with hydrocyanic acid, cyanogen chloride, and the oxides of nitrogen. It thus has the power of holding acid as well as basic compounds in combination. Zirconium, on the other hand, the element next in succession to titanium, exhibits no such reactions, and its combinations seem limited to compounds of a basic character, as work now in progress in this laboratory indicates. We might then assume the rule "that in the first sub-group the reactivity decreases with a rise in atomic weight, being highest in titanium," with more or less reason. In the case of the opposite sub-group, however, the paucity of data forbids the formulation of any such law. Tin we know to be exceedingly reactive in its quadrivalent haloids, but germanium, the element which precedes it in the sub-group, whose reactions, if studied, would make some such general statement possible, has been but little investigated with such an end in view.

The subsequent chlorides of thorium and lead are being studied at present, and the determination of their reactions will show the relevance of their weight relationship to their behaviors, and make possible a more comprehensive and thorough comparison of the actions of the tetrachlorides of the fourth periodic group. The accompanying table represents the behavior of the several tetrachlorides towards various reagents. The reactivity is indicated by the letter "r," and the failure to form compounds with these reagents by the character "o."

	Aniline, etc.	Fatty amines.	Urea, thiourea	Acid amides.	HCN.	Acetonitrile.	Benzonitrile.	Tolunitrile.	Succinonitrile.	Chlorcyanog'n	S <sub>2</sub> Cl <sub>2</sub> .	NO <sub>2</sub> .	PCl <sub>5</sub> .	PCl <sub>3</sub> .	NH <sub>3</sub> .
CCl <sub>4</sub> .....	r	.	.	.	.	.	.	.	.	.	.	r	.	.	r
SiCl <sub>4</sub> .....	r	r	r	o	o	o	o	o	o	o	o	o	o	o	r
TiCl <sub>4</sub> .....	r	.	.	.	r	r	r	r	r	r	r	.	r	.	r
GeCl <sub>4</sub> .....	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
ZrCl <sub>4</sub> .....	r	r	.	.	o	o	o	o	o	o	.	.	.	.	r
SnCl <sub>4</sub> .....	r	r	.	.	r	r	r	r	r	o	r	.	r	.	r
PbCl <sub>4</sub> .....	r	.	.	.	.	.	.	.	.	.	.	.	.	.	r
ThCl <sub>4</sub> .....	r	.	.	.	.	.	.	.	.	.	.	.	.	.	r

#### THE ACTION OF AROMATIC AMINES AND NITRILES ON SILICON TETRACHLORIDE.

The work was entered upon chiefly with a view to developing some new analogies between the behavior of silicon tetrachloride and that of the tetrachlorides of the other members of Group IV, or any characteristic differences which might prove noteworthy. The hope of the investigation was, that by some well defined series of reactions observed therein, a new means might be found of isolating the members of the group, in their higher forms of combination, from one another or from members of other groups.

The investigation is all the more demanded, since but little work has been done in this field, the action of nitriles having been studied only with the tetrachlorides of titanium and tin.<sup>1</sup> The action, therefore, of nitriles on silicon tetrachloride was a needed expansion of the subject, and this, together with the actions of the chlorides of sulphur and phosphorus, cyanogen and chloride of cyanogen, nitrogen dioxide and nitroxyl chloride, upon silicon tetrachloride, constitute the experimental part of the present research, while the demonstration of the inactivity of the latter, as compared with the behaviors of tin and titanium tetrachlorides, determines its scope.

The second part of this article deals with the reactions between silicon tetrachloride and amines of the benzene series. The behavior of these bodies towards higher haloids of the fourth group has been investigated only in the silicon derivatives, and

<sup>1</sup> Henke: *Ann. Chem. (Liebig)*, 106, 281; Shinn: Thesis, University of Pennsylvania, 1895.

here the reaction cannot be said to be determined, since the investigators in this field are at odds in their results, and it is hoped that this work will aid in fixing the exact constitution of the products of the reaction of silicon tetrachloride and aromatic amines.

The silicon tetrachloride was made by the action of dry chlorine on silicon, at a low heat, the resulting vapors being collected in chilled condensers. Any free chlorine was removed from the product by shaking with mercury, and the silicon tetrachloride further purified by fractional distillation, till it exhibited the constant boiling-point,  $57^{\circ}$ – $59^{\circ}$ . The silicon used in this preparation was made by the reduction of very fine sand, free from iron, by magnesium powder, according to the method recommended by Gattermann.

#### THE ACTION OF FORMONITRILE ON SILICON TETRACHLORIDE.

Dry hydrocyanic acid gas conducted into cooled silicon tetrachloride produces no change; no product is formed and the silicon tetrachloride boils at the usual temperature. Wöhler<sup>1</sup> had prepared the compound  $\text{TiCl}_4 \cdot 2\text{HCN}$ , while Klein<sup>2</sup> got a corresponding tin derivative, as did also Shinn.<sup>3</sup> These results led to the attempt to combine formonitrile and silicon tetrachloride with the result above indicated.

#### ACETONITRILE.

Henke<sup>4</sup> had shown that methyl cyanide combined with titanium and tin tetrachlorides, to form derivatives of the type  $\text{SnCl}_4 \cdot 2\text{CH}_3\text{CN}$ . Anhydrous acetonitrile, made by the distillation of acetamide and phosphorus pentasulphide, and further purification of the product, was added to silicon tetrachloride chilled in ice; no action was apparent or heat generated. The precaution of chilling in ice was taken, because in the case of tin derivatives the amount of heat produced in the reaction was sufficient to decompose the products. Here, however, even when the ordinary temperature was resumed, no combination was effected. The slightest trace of moisture, however, serves

<sup>1</sup> *Ann. Chem.* (Liebig), 73, 226.

<sup>2</sup> *Ann. Chem.* (Liebig), 74, 86.

<sup>3</sup> Thesis, University of Pennsylvania, 1896.

<sup>4</sup> *Ann. Chem.* (Liebig), 106, 281.

to precipitate a silica compound which retains the nitrile tenaciously. Its analysis, however, indicates no definite constitution, and it is probably nothing more than a mixture of silicic acid and methyl cyanide.

#### PROPIONITRILE.

This was made by the distillation of potassium cyanide with potassium ethyl sulphate; the isopropionitrile formed at the same time, being removed by a small quantity of concentrated hydrochloric acid. As with acetonitrile, the anhydrous liquid gives no compound with silicon tetrachloride, while the tetrachlorides of tin and titanium afford derivatives of a constitution similar to the acetonitrile bodies. (See above references.)

#### SUCCINONITRILE.

The nitrile of succinic acid was made by digesting ethylene dibromide with an alcoholic solution of potassium cyanide, and after being rendered absolutely anhydrous was added to silicon tetrachloride. It gave no derivative, being in this distinguished from tin, which forms the compound  $\text{SnCl}_4 \cdot 2(\text{CH}_2\text{CN})$ .<sup>1</sup>

#### AROMATIC NITRILES. BENZONITRILES.

This reagent was made by distilling benzoic acid and dry potassium thiocyanate, adding ammonia to the semi-solid distillate and extracting with ether. With this nitrile the behavior of tin and titanium chlorides had been investigated by Henke,<sup>2</sup> who obtained the compounds  $\text{C}_6\text{H}_5\text{CN} \cdot \text{TiCl}_4$  and also  $\text{C}_6\text{H}_5\text{CN} \cdot \text{SnCl}_4$ . With silicon tetrachloride, however, it gives no derivative under ordinary conditions or by the action of heat and pressure. Silicon tetrafluoride also exhibits no reaction with this nitrile.

#### TOLUNITRILE.

The tetrachloride here gives a compound, but neither the chloride nor fluoride of quadrivalent silicon unite with it. No variation in the result was noticed when the silicon tetrachloride was heated under pressure with the nitrile, these compounds remaining uncombined as before.

<sup>1</sup> Shinn: University of Pennsylvania, Thesis, 1896.

<sup>2</sup> *Ann. Chem.* (Liebig), 106, 181.

The *nitriles* of *mandelic* and *lactic acids* gave no derivatives with silicon tetrachloride under ordinary conditions, but when heated under pressure, silicic acid and complex tarry decomposition products resulted, which did not attract analysis. In all the above cases the mediums of interaction were benzene and ether, the latter being preferable, because it was thought the more easily dried.

#### NITROGEN DIOXIDE.

Marignac<sup>1</sup> obtained the derivative of carbon tetrachloride, to which he assigned the formula  $\text{CCl}_4 \cdot 2\text{NO}_2$ . Later, Kuhlmann<sup>2</sup> prepared derivatives of silicon tetrachloride with every oxide of nitrogen. On passing  $\text{NO}_2$ , prepared by heating lead nitrate, into silicon tetrachloride, no heat development was noticed. The latter dissolves the gas and becomes colored by the same, but a single distillation, during which the boiling-point showed no change, sufficed to completely decolorize the liquid and remove the nitrogen dioxide from it.

#### THE MIXED VAPORS OF $\text{NO}_2$ AND CHLORINE.

These were conducted into cooled silicon tetrachloride, as in the former instance. There was no liberation of heat, the liquid becoming merely colored by the gases and giving them up freely on distillation, the boiling-point remaining normal, thus indicating that no compound had been formed and that simply an absorption of the vapors had taken place. This is all the more remarkable, since the derivatives  $3\text{TiCl}_4 \cdot 2\text{NO}_2 \cdot \text{Cl}$  and  $3\text{SnCl}_4 \cdot 2\text{NO}_2 \cdot \text{Cl}$  had been readily prepared by Hampe.<sup>3</sup>

#### THE CHLORIDES OF PHOSPHORUS.

Phosphorus trichloride, under ordinary conditions, or heated under pressure with silicon tetrachloride, gives no derivative; the liquids merely commingle to a solution from which both constituents may be isolated by fractional distillation. Phosphorus in solid condition remains insoluble in silicon tetrachloride, but when its vapors, partly dissociated, are conducted into the same, they are absorbed and dissolved. Upon subsequent distillation

<sup>1</sup> *Ann. Chem.* (Liebig), 38, 17.

<sup>2</sup> *Ann. Chem.* (Liebig), 39, 320.

<sup>3</sup> *Ann. Chem.* (Liebig), 126, 43.



the liquid, for the greater part, boils at  $58^{\circ}$ – $60^{\circ}$ , leaving a liquid residue, which is driven over only at the boiling-point of phosphorus trichloride. The only effect of the phosphorus pentachloride seems to be a slight elevation of the boiling-point of the silicon compound, while the latter serves to completely dissociate the pentachloride into the lower chloride and free chlorine. Casselmann<sup>1</sup> had prepared a compound of tin and phosphorus chloride, of the formula  $(\text{SnCl}_4)_2 \cdot \text{PCl}_5$ . Here again the analogy between tin and silicon fails.

#### SULPHUR MONOCHLORIDE.

The liquids were mixed in all proportions, and on boiling the mixture, the silicon tetrachloride being in excess, the greater part came over between  $57^{\circ}$ – $59^{\circ}$ . The temperature rises gradually and then suddenly is elevated to  $139^{\circ}$ , the boiling-point of sulphur monochloride, thus showing that no compound had been formed. H. Rose,<sup>2</sup> however, obtained the compound  $\text{SnCl}_4 \cdot 2\text{S}_2\text{Cl}_2$ .

#### CYANOGEN CHLORIDE.

A saturated solution of mercuric cyanide was made, and an excess of the salt was added to this in a finely divided condition. Chlorine was then conducted into this liquid, until it was completely saturated by the gas, and the product was set aside in a dark place in a flask, filling the space above the liquid with chlorine. After a time the excess of mercuric cyanide had dissolved and the chlorine was completely absorbed. Uncombined chlorine was then removed by shaking with mercury, and the solution was poured into a flask provided with a calcium chloride tube. On gently heating the solution, the cyanogen was evolved, and led through a tube filled with copper turnings, to remove the last traces of chlorine, into silicon tetrachloride chilled in ice and salt. Silicon in its behavior here was found to ally itself with tin, both Wöhler<sup>3</sup> and Klein<sup>4</sup> having failed to obtain chlorcyanogen compounds with the higher chlorides of the latter, while Wöhler had however succeeded in preparing a titanium derivative of the composition  $\text{TiCl}_4(\text{CNCl})_2$ .

<sup>1</sup> *Ann. Chem.* (Liebig), 83, 258.

<sup>2</sup> *Pogg. Annalen*, 42, 517.

<sup>3</sup> *Ann. Chem.* (Liebig), 74, 86.

<sup>4</sup> *Ann. Chem.* (Liebig), 73, 221.

## SILICON TETRACHLORIDE AND AROMATIC AMINES.

Knop<sup>1</sup> obtained derivatives from silicon tetrafluoride with urea and aniline. With the latter a white crystalline compound was prepared, to which he assigned the formula  $\text{Si}_2\text{H}_2\text{F}_4 \cdot 3\text{C}_6\text{H}_5\text{N}$ . This constitutes the first work investigating the action of the aromatic amines on the tetrahaloids of the fourth group. As, however, the medium here used is anhydrous alcohol which decomposes the silicon tetrafluoride, the resulting compound cannot be said to be a derivative of it. Laurent and Delbos<sup>2</sup> obtained a compound of aniline and silicon tetrafluoride, whose constitution they expressed as  $3\text{C}_6\text{H}_5\text{NH}_2 \cdot 2\text{SiF}_4$ , but did not establish. Jackson and Comey<sup>3</sup> obtained also this compound, proved its constitution, and described its properties. They prepared in a similar manner, derivatives from ortho- and para-toluidine, diphenylamine and dibenzylamine, while dimethylaniline and quinoline gave no product.

Girard and Pabst<sup>4</sup> investigated the action of the tetrachlorides of carbon, tin, and silicon on aniline at increased temperatures. With carbon tetrachloride and aniline, they obtained the derivatives, triphenylguanidine and rosaniline. With the chloride of tin under the same conditions, violaniline, mauvaniline (phenyl-safranine), and, it seems, rosaniline were obtained. Silicon tetrachloride also forms violaniline, together with the production of triphenylamine blue.

The only investigations on these reactions which are established by exact analyses are those of Harden<sup>5</sup> and Reynolds<sup>6</sup>; the latter is a repetition of the work of the former experimenter, in which results are obtained which vary from it. Unaware of any conflict of results, or, indeed, of any precedence in the field, the present investigation was begun; and it was not until its results were complete that any divergence in previous work on the subject was encountered. The work was then found to agree entirely with that of the earlier of these investigators, and to establish by new methods of procedure his results.

<sup>1</sup> *Chem. Centrbl.*, 1858, 388: *Jsb. d. chem.*, 1858, 148: *J. prakt. Chem.*, 74, 41.

<sup>2</sup> *Ann. chim. phys.*, 22, 101.

<sup>3</sup> *Ber. d. chem. Ges.*, 19, 3194.

<sup>4</sup> *Bull. Soc. Chim.*, 34, 38.

<sup>5</sup> *J. Chem. Soc.*, 51, 40.

<sup>6</sup> *J. Chem. Soc.*, 55, 474.

## SILICON TETRACHLORIDE AND ANILINE.

When aniline is added to silicon tetrachloride, there is a great evolution of heat, with the coincident precipitation of a white compound completely insoluble in ether. Owing to the violence of the reaction, anhydrous ether, and afterwards benzene, was used as a diluent and medium of interaction. The complete combination of the silicon tetrachloride was evidenced by the loss of the odor of that body when sufficient aniline had been added. With this as a means of indication, the synthetic proportions were found to be one molecule of silicon tetrachloride to four molecules of aniline.

Three and five-tenths grams silicon tetrachloride required 7.50 grams aniline. Calculated, 7.65 grams aniline.

Five and eight-tenths grams silicon tetrachloride required 12.4 grams aniline. Calculated, 12.68 grams aniline.

That the silicon tetrachloride united with the aniline in the proportion of one to four molecules, was further proved by weighing the resultants of the action of quantities of these substances united according to the above ratio. Ether was used as a medium.

To three and five-tenths grams of silicon tetrachloride, dissolved in ether, a slight excess of four molecules of aniline was added, stirring vigorously during the addition of the latter substance. The white precipitate thus obtained was placed on a tared filter and washed with anhydrous ether, in a current of dry air, until the washings showed no trace of aniline. The precipitate was then dried in a desiccator, the filter and precipitate placed in a weighing bottle and its weight found.

From three and five-tenths grams silicon tetrachloride were obtained 11.16 grams product. Calculated for three and five-tenths grams silicon tetrachloride, and 7.66 grams, or four molecules of aniline, gave 11.3 grams product.

In a second experiment the following figures were obtained:

Four and six-tenths grams of silicon tetrachloride gave 14.8 grams product. Calculated for 4.60 grams silicon tetrachloride and 10.06 grams, or four molecules of aniline, 14.66 grams product.

The additional weight of the precipitate was here probably due

to some small quantities of aniline retained by it. Portions of this substance which had been placed in the cup of a Soxhlet apparatus and washed with ether for three hours, were taken for analysis. The exit tube of the Soxhlet apparatus was, in this instance, connected with a drying apparatus, and the precipitate during the washing thus protected from the action of moist air. All precautions were taken to remove every trace of free aniline, the washings of the precipitate being constantly examined for the same, till they failed to give reactions of that body. The compound was placed in a desiccator and portions taken for analysis.

I. 0.1135 gram gave 0.0122 gram silica, or 5.052 per cent. silicon.

II. 0.3739 gram gave 0.0280 gram silica, or 4.80 per cent. silicon.

III. 0.0965 gram gave 0.0103 gram silica, or 5.01 per cent. silicon.

IV. 0.1432 gram gave 0.2805 gram carbon dioxide, or 53.42 per cent. carbon ; and 0.0684 gram water, or 5.31 per cent. hydrogen.

V. 0.2153 gram gave 0.1572 gram Pt, or 10.47 per cent. nitrogen.

VI. 0.2034 gram gave by Dumas' method 0.02166 gram nitrogen, or 10.65 per cent. nitrogen.

VII. 0.3467 gram gave 0.3710 gram silver chloride, or 26.46 per cent. chlorine.

VIII. 0.2972 gram gave 0.3130 gram silver chloride, or 26.05 per cent. chlorine.

	Calculated for (C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>4</sub> SiCl <sub>4</sub> .	I.	Found. II.	III.
Silicon .....	5.16	5.05	4.80	5.01
Carbon .....	53.13	53.42	....	....
Hydrogen .....	5.16	5.31	....	....
Nitrogen .....	10.32	10.47	10.65	....
Chlorine .....	26.19	....	26.46	26.05

These analyses further substantiate the proportions of combination which had been indicated by the synthetic experiments. As the compounds thus produced possess the formula

$\text{SiCl}_4(\text{C}_6\text{H}_5\text{NH}_2)_4$ , the reaction may be written as follows:



This was regarded as a single molecular compound, and the reaction was thus written until the use of a medium other than benzene, in the combination of these bodies, gave results that pointed to the conclusion that the above compound was a mixture of the compounds  $\text{SiCl}_4(\text{C}_6\text{H}_5\text{NH}_2)_4$  and  $2\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$ , so formed by the combination of one molecule of silicon tetrachloride and four of aniline. The resulting dichlorosilicon diphenylamide and the aniline hydrochloride, being both insoluble in ether, would be combined in such proportions as to give a mixture whose total composition would correspond to the formula deduced from the above analysis:



The results that led to the inference that the latter compound was not simple are below detailed. When instead of ether as a medium, anhydrous benzene is used, all of the products are not precipitated, but it was found on washing the precipitate thus obtained with benzene in a dry Soxhlet apparatus, a white compound was left, which gave the following proportions on analysis:

I. 0.3401 gram gave 0.3751 gram silver chloride, or 26.99 per cent. chlorine.

II. 0.2266 gram gave 0.2506 gram silver chloride, or 27.07 per cent. chlorine.

The compound thus obtained did not show any silica content.

	Calculated for aniline hydrochloride.	I.	Found. II.
Chlorine.....	27.13	26.99	27.07

It was further noticed that the total weight of this precipitate was only about half that calculated for the complete precipitation of the compound of silica, expressed in the reaction with ether as a medium.

I. Three and five-tenths grams silicon tetrachloride and four molecules of aniline gave 5.29 grams of product insoluble in benzene; with ether as a medium obtained 11.3 grams of product insoluble in ether.

II. Three and nine-tenths grams silicon tetrachloride gave 5.06 grams of product insoluble in benzene; calculated for  $(C_6H_5NH_2)_3SiCl_4$ , 12.43 grams.

As the aniline hydrochloride was entirely free from silica, the silicon compound produced in the reaction was looked for in the clear filtrate from the aniline hydrochloride. This solution was not allowed to evaporate, to yield in this manner the dissolved derivative, as it was known, since the aniline was originally in slight excess, that any compound so produced would be saturated with aniline, the last traces of which it would be difficult to remove. To the solution was therefore added ether, which precipitated a white compound containing silicon, carbon, hydrogen, nitrogen and chlorine, and whose analyses gave the following results:

I. 0.2461 gram substance gave 0.4602 gram carbon dioxide, or 50.95 per cent. carbon; and 0.0860 gram water, or 3.88 per cent. hydrogen.

II. 0.2840 gram gave 0.0589 gram silica, or 9.69 per cent. silicon.

III. 0.2131 gram gave 0.0442 gram silica, or 9.74 per cent. silicon.

IV. 0.2761 gram gave 0.2788 gram silver chloride, or 24.70 per cent. chlorine.

V. 0.3013 gram gave 0.2014 gram Pt, by method of Varrentrapp and Will, or 9.59 per cent. nitrogen.

	Calculated for $SiCl_4(C_6H_5NH_2)_3$	I.	Found.	II.
Carbon.....	50.88	50.95		...
Hydrogen.....	4.24	3.88		....
Nitrogen.....	9.87	9.59		....
Silicon.....	9.87	9.69		9.74
Chlorine.....	25.08	....		24.70

This is the compound which had been obtained by Harden<sup>1</sup>. On weighing the amount of this produced from definite amounts of silicon tetrachloride, and adding to it the quantity of aniline hydrochloride produced at the same time, the total weight both of the silicon tetrachloride and the aniline are united and found in the products described above.

<sup>1</sup> *J. Chem. Soc.*, 51, 40.

Three and five-tenths grams of silicon tetrachloride and four molecules, or 7.65 grams, aniline gave :

	Grams.
Dichlorosilicon diphenylamide.....	5.83
Aniline hydrochloride.....	5.29
	<hr/>
Total found .....	11.12
Calculated for three and five-tenths grams silicon tetra- chloride and 7.65 aniline.....	11.15

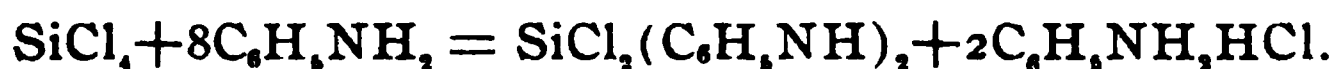
Three and nine-tenths grams silicon tetrachloride and 8.55 grams aniline gave :

	Grams.
Dichlorosilicon diphenylamide.....	6.52
Aniline hydrochloride.....	5.96
	<hr/>
Total found.....	12.58
Calculated for three and nine-tenths grams silicon tetrachloride and 8.53 grams aniline.....	12.43

These bodies are almost quantitatively produced, as the above results have indicated, and no amount of any secondary products can be believed to be present. The reaction may, therefore, be written as follows :



Both these products were obtained, and only these, although the aniline was always in excess ; while Reynolds writes the reaction thus :

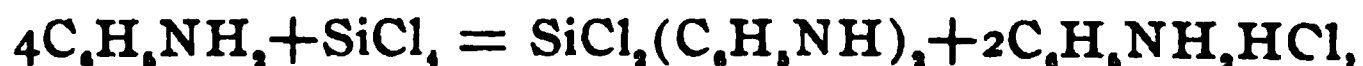


The silicon tetraphenylamide prepared by him is a well crystallized body, and the careful methods of analysis pursued place its exact constitution beyond doubt. The cause of the divergence in the results is, therefore, due to the variation in procedure. In the work of Harden in the present investigation, smaller quantities of material are used (only a slight excess of four molecules of aniline are employed), and the diluents of the action were not present in such great amount as in the work of Reynolds, where the benzene is double the value of the reagents. In his work, 100 grams of silicon tetrachloride are added to 438 grams of aniline, or in the proportion of one to eight molecules.

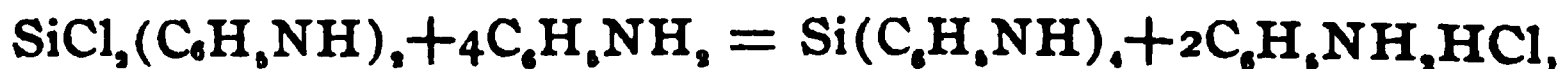
In the use of such a quantity of benzene, the purpose is to keep the larger amount of the silicon compound in solution, so that the precipitate will consist almost wholly of aniline hydrochloride, retaining but little of the silicon derivative. The precipitate, according to the method of this investigator, is quickly filtered from the solution, washed often with benzene and the filtrate distilled free from the greater part of the benzene in a current of hydrogen. The syrupy liquid thus obtained was poured into an excess of carbon disulphide, which served to precipitate a little aniline hydrochloride which had continued in solution. The filtrate was then concentrated and allowed to crystallize, when the compound described by him was obtained.

It will be here observed that the work is less direct than that of the methods of procedure before described, and that more chance of secondary reactions is encountered in the manipulation than in the first instance, and that the reaction which requires four molecules of aniline with one of silicon tetrachloride, represents the normal behavior of these two substances.

It is believed that the use of ether in lieu of benzene, furnishes a far preferable medium for determining the proportions of the reaction, though preventing an analysis of the two products, which are equally insoluble in it. It renders possible, however, a weighing of the total products of the reaction and a comparison of their quantity, with the amount of silicon tetrachloride and aniline used, since it exerts no solvent action on either product, while both reagents are soluble in it. The possibility of secondary reactions, or of the solvent playing the rôle of a reagent, was thus avoided. The readiness of weighing the total product of the reaction, and the determination of the synthetic proportions of the same, seem to establish that it proceeds as follows :



and that the compound without chlorine,  $\text{Si}(\text{C}_6\text{H}_5\text{NH})_4$ , and the reaction which Reynolds writes, does not represent the immediate action of the reagents, but that the time-consuming method of the latter introduces a second phase into the reaction, during which the following may take place :





which would explain the formation of both silicon derivatives and the contradiction of the reactions.

It might here be noticed that the names "Dichlorosilicon diphenylamide" for  $\text{SiCl}_2(\text{C}_6\text{H}_5\text{NH})_2$ , and "Silicon tetraphenylamide" for  $\text{Si}(\text{C}_6\text{H}_5\text{NH})_4$ , are cumbrous and not sufficiently clear; "Chlorsilicon dianilide," for the first, and "Silicon tetranilide" for the latter, are suggested as briefer and more expressive names.

#### SILICON TETRACHLORIDE AND ORTHOTOLUIDINE.

The methods employed in the preparation of the toluidine derivatives were similar to those made use of in the production of the aniline compound. A greater reactivity was, however, noticed on the part of the toluidine, as it was found to combine with the silicon tetrachloride at the temperature of ice and salt, while aniline was inert under these conditions. The precaution was taken to remove all paratoluidine from the liquid variety, by means of their acetyl derivatives, and the pure orthotoluidine thus formed was used in the reactions.

The white compound insoluble in benzene was washed with ether, dried, and analyzed.

I. 0.3146 gram gave 0.3126 gram silver chloride, or 24.32 per cent. chlorine.

II. 0.4012 gram gave 0.4006 gram silver chloride, or 24.43 per cent. chlorine.

Calculated for  $\text{C}_6\text{H}_4\text{CH}_3\text{NH}_2\text{HCl}$ , 24.73 per cent. chlorine.

The compound is, therefore, toluidine hydrochloride and its production similar to that of the aniline body.

On the addition of ether to the filtrate, a white voluminous precipitate appeared, which was washed with anhydrous ether, and dried in a desiccator. Of this substance :

I. 0.1722 gram gave 0.0319 gram silica, or 8.70 per cent. silicon.

II. 0.1650 gram gave 0.0313 gram silica, or 8.91 per cent. silicon.

III. 0.2160 gram gave 0.0403 gram silica, or 8.77 per cent. silicon.

IV. 0.1834 gram gave 0.1727 gram silver chloride, or 22.51 per cent. chlorine.

V. 0.2803 gram gave 0.2617 gram silver chloride, or 22.85 per cent. chlorine.

	Calculated for $\text{SiCl}_4(\text{C}_6\text{H}_4\text{CH}_2\text{NH})_2$ .	I.	Found. II.	III.
Silicon .....	9.00	8.70	8.91	8.77
Chlorine .....	22.80	22.51	22.85	....

The behavior of orthotoluidine is, therefore, analogous to that of aniline. That four molecules of toluidine were required for the saturation of silicon tetrachloride was proved as in the former instance by determining the synthetic proportions of the compounds, and by the use of ether as a medium, determining the weight of the total product. It required :

	Toluidine. Grams.
For 3.0 grams silicon tetrachloride.....	7.7
Calculated.....	7.6
For 5.3 grams silicon tetrachloride.....	13.2
Calculated .....	13.2

The precipitate produced and washed in ether in the

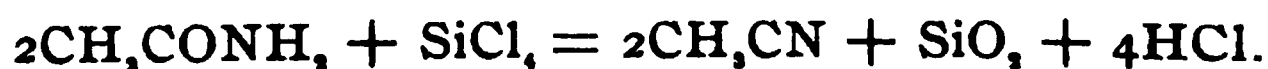
	Product. Grams.
First experiment gave.....	10.8
Calculated for 7.6 and 3.0 .....	10.6
Second experiment gave.....	18.8
Calculated for 5.3 and 13.2 .....	18.5

#### SILICON TETRACHLORIDE AND ACID AMIDES. BENZAMIDE.

The vapors of silicon tetrachloride, conducted into benzamide in the molten condition, gave rise to benzaldehyde, which was collected and recognized by the malachite green reaction. It was thought that the silicon tetrachloride would form a product with the benzamide, as with the aromatic amines, but it is probable that the benzamide is not sufficiently basic in character to so act.

#### SILICON TETRACHLORIDE AND ACETAMIDE.

With the latter compound no derivative is obtained, but on conducting the vapors into acetamide, acetonitrile was produced. Possibly according to the following :



The present investigation on the behavior of silicon tetrachloride is but one in a series which has for its scope the determination of the reactions also of lead and tin tetrachlorides with amine bodies. Work is also in progress in this laboratory on the conduct of thorium and zirconium tetrachlorides with the same reagents. The results thus obtained will afford a wider study of the fourth group elements, and furnish data for a broader comparison of the reactions of its members.

## SOME NEW RUTHENOCYANIDES AND THE DOUBLE FERROCYANIDE OF BARIUM AND POTASSIUM.

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THE resemblance between the double cyanides of iron, ruthenium, and osmium, was first pointed out by Claus,<sup>2</sup> and further developed by Martius,<sup>3</sup> who formed a number of the double osmocymanides. More recently Dufet<sup>4</sup> has described the crystals of potassium ruthenocyanide and osmocyanide and shown their close crystallographic resemblance to the ferrocyanide. The chemistry and the crystallography of the ferrocyanides has been very exhaustively studied by Wyruboff,<sup>5</sup> and his work affords a valuable starting point for any investigation of the isomorphous ruthenocyanides and osmocyanides.

Since the publication of a recent paper by one of us (Howe)<sup>6</sup> on the ruthenocyanides, several new salts have been prepared, and in all of them the analogy of the ruthenocyanides with the ferrocyanides is complete. The ruthenocyanides are decidedly more soluble than the ferrocyanides and correspondingly more difficult to crystallize. In one salt only have crystals been obtained which were perfect enough to measure.

*Strontium Ruthenocyanide*,  $\text{Sr}_2\text{Ru}(\text{CN})_{12} \cdot 15\text{H}_2\text{O}$ .—Formed by treating lead ruthenocyanide with dilute sulphuric acid and neutralizing of the hydorruthenocyanic acid formed with strontium

<sup>1</sup> Contributed to the November meeting of the Cincinnati Section of the American Chemical Society, November 16, 1897.

<sup>2</sup> Beiträge zur Chemie der Platinmetalle. pp. 98 and ff.

<sup>3</sup> Ueber die Cyanverbindungen der Platinmetalle. Inaug. Diss., Göttingen, 1860.

<sup>4</sup> Compt. rend., 120, 377.

<sup>5</sup> Ann. chim. phys. [4], 16, 280: 21. 271.

<sup>6</sup> This Journal, 18, 981.

hydroxide. The salt obtained by treating "Prussian purple," the ruthenium analogue of Prussian blue, with strontium hydroxide, could not be obtained in a pure condition. Pale straw-colored, elongated plates, probably monoclinic, very soluble in water, and quite efflorescent. By adding alcohol to its hot solution, the salt can be obtained in long, fine needles. It is very difficult to obtain a salt pure enough for analysis, and owing to efflorescence the water determination is low. The corresponding strontium ferrocyanide crystallizes with fifteen molecules of water of crystallization.<sup>1</sup>

## ANALYSIS.

I. Crystallized from water.		II. Crystallized from dilute alcohol.	
Calculated for		Found.	
$\text{Sr}_2\text{Ru}(\text{CN})_{12} \cdot 15\text{H}_2\text{O}$		I.	II.
Water.....	38.41	36.80	37.12
Ruthenium ....	14.45	14.36	....
Strontium.....	24.94	25.11	....

*Barium Potassium Ruthenocyanide*,  $\text{K}_2\text{BaRu}(\text{CN})_{12} \cdot 3\text{H}_2\text{O}$ .—Formed by mixing equivalent solutions of the barium and potassium salts; also, mixed with the barium salt, by treating Prussian purple with barium hydroxide. Crystallizes best from its hot solution in water while evaporating on the water-bath. Pale amber to colorless rhombohedra, hardly distinguishable from the corresponding ferrocyanide, but quite soluble in water. The salt is difficult of analysis, owing to the difficulty of completely decomposing it by heat to obtain the insoluble oxide of ruthenium. Some of the ruthenium invariably went into solution in hydrochloric acid, and from this solution a blue precipitate, insoluble in acids, soon separated, probably  $\text{Ru}(\text{CN})_6$ , but invariably containing both barium and potassium.

## ANALYSIS.

Calculated for		Found.			
$\text{K}_2\text{BaRu}(\text{CN})_{12} \cdot 3\text{H}_2\text{O}$		I.	II.	III.	IV.
Potassium .....	14.83	12.98	....	14.51	13.16
Barium.....	26.07	27.38	25.31	....	25.83
Ruthenium.....	19.27	18.71	....	....	18.94
Water .....	10.25	10.19	10.80	10.83	10.99

The water in I was determined by loss, but in the other three analyses by absorption and direct weighing. In these three

<sup>1</sup> Wyruboff: *Ann. chim. phys.*, 16, 287.

cases the salt in a closed tube was heated until it began to decompose. It is therefore impossible that the salt can contain five molecules of water, as this would require sixteen per cent.

Wyrouboff<sup>1</sup> describes the barium potassium ferrocyanide as  $K_2BaFe(CN)_6 \cdot 5H_2O$ , but crystallographically the two salts resemble each other very closely.

Crystallography of barium potassium ruthenocyanide,  $K_2BaRu(CN)_6 \cdot 3H_2O$ . Rhombohedral.  $a : c = 1.558$ . Angle between basal plane and rhombohedron  $= 119^\circ 4'$ . The mean of thirty-nine measurements on eight crystals gave  $81^\circ 27'$  as the rhombohedral angle. (Calculated  $= 81^\circ 36'$ .)

Crystals rhombohedral, with occasional development of basal plane. Rhombohedral faces usually appear pitted, and give a bundle of reflections, making a variation of  $50'$  in the measured angles; optically negative; double refraction weak. In converging polarized light the cross opens slightly into hyperbolas.

A comparison of the crystallography of the ruthenocyanide with the ferrocyanide as given by Wyrouboff shows their close relationship.

Barium potassium ferrocyanide.<sup>2</sup>

Rhombohedral.  $a : c = 1.570$ .

Angle between basal plane and rhombohedron  $= 118^\circ 53'$ .

Rhombohedral angle  $= 98^\circ 48'$  ( $81^\circ 12'$ ).

Optically positive.

Barium potassium ruthenocyanide.

Rhombohedral.  $a : c = 1.558$ .

Angle between basal plane and rhombohedron  $= 119^\circ 4'$ .

Rhombohedral angle  $= 81^\circ 36'$  (calculated);  $81^\circ 27'$  (measured).

Optically negative.

*Barium Cesium Ruthenocyanide*,  $Cs_2BaRu(CN)_6 \cdot 3H_2O$ .—When barium ruthenocyanide is mixed with half the equivalent of cesium sulphate, there separate from the solution, even before it can be filtered from the barium sulphate, unless very dilute, minute, brilliant, yellowish-white to colorless crystals, which under the microscope appear as rhombohedra, with angle of about  $83^\circ$ , and in every way resembling the barium potassium salt, except that the basal plane predominates. They are very insoluble even in hot water, and cannot be recrystallized owing to partial decomposition and precipitation of a blue insoluble

<sup>1</sup> Wyrouboff: *Ann. chim. phys.*, 21, 279.

<sup>2</sup> Wyrouboff: *loc. cit.*

substance, probably  $\text{Ru}(\text{CN})_6$ . The salt is stable in the air as analyses II and III were made from a salt which had stood exposed in the laboratory for several weeks.

#### ANALYSIS.

	Calculated for $\text{Cs}_2\text{BaRu}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ .	I.	Found. II.	III.
Cesium.....	37.18	....	....	36.45
Barium .....	19.21	19.06	....	18.70
Ruthenium .....	14.21	....	....	14.33
Water (by loss at $120^\circ$ )....	7.56	7.64	7.31	7.51

The sodium, the magnesium, and the calcium salts have been obtained, but are very difficult to crystallize, owing to their great solubility. The magnesium salt forms very pale green crystals, which are very efflorescent.

The strontium potassium, and the strontium cesium ruthenocyanide have been formed, but not in pure enough condition for analysis. They seem to resemble the barium double salts under the microscope and bear no resemblance to the salt  $\text{K}_2\text{SrFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , described by Wyruboff, which crystallizes in prismatic monoclinic crystals. The strontium rubidium ruthenocyanide gives a precipitate on warming its solution, and thus appears to resemble the strontium potassium ferrocyanide which precipitates the anhydrous salt under similar circumstances.

Analysis having shown that the barium potassium ruthenocyanide contains three molecules of water of crystallization, and yet resembles closely the ferrocyanide to which Wyruboff<sup>1</sup> gives five molecules, a re-examination of the ferrocyanide was made. Bunsen, who first made the salt, gives the formula with three molecules of water, and from analogy to the ruthenocyanide three would be expected. Further, Martius<sup>2</sup> formed the corresponding osmocyanide, to which he gives the formula  $\text{K}_2\text{BaOs}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ . His description of the salt would hold equally good for the ruthenocyanide or ferrocyanide, except that it is efflorescent.

A considerable quantity of the ferrocyanide was prepared in this laboratory by Mr. H. W. Drake. The very sparingly soluble barium salt was made by the action of barium chloride on potassium ferrocyanide, and this, mixed with an equivalent

<sup>1</sup> Wyruboff: *Loc. cit.*

<sup>2</sup> Martius: *Cyanverbindungen*, p. 23.

quantity of the potassium salt was dissolved in a large amount of water. On evaporation and cooling the barium potassium salt was deposited in pale straw-colored rhombohedra, often several millimeters across. The salt, contrary to the statement of Wyruboff, is perfectly stable, and after five months' exposure to the air the crystals are perfectly clear and the surfaces bright. Measurement of the crystal angles, and examination of the optical properties, showed the salt to be identical with that described by Wyruboff. Analysis showed that the salt has *three* molecules of water of crystallization, and its formula is  $K_2BaFe(CN)_{11} \cdot 3H_2O$ . The water was determined directly by absorption in a calcium chloride tube, the salt being heated until decomposed.

## ANALYSIS.

	Calculated for $K_2BaFe(CN)_{11} \cdot 3H_2O$ .	Calculated for $K_2BaFe(CN)_{11} \cdot 3H_2O$ .	Found. I.	Found. II.
Water.....	17.40	11.38	11.68	11.72
Barium ....	26.55	28.53	28.88	28.61

*Barium Cesium Ferrocyanide*,  $Cs_2BaFe(CN)_{11} \cdot 3H_2O$ . This salt, which appears never to have been described, was made for purposes of comparison. It was formed by decomposing barium ferrocyanide with half the equivalent of cesium sulphate in very dilute solution. It crystallizes in very small, slightly yellowish-white rhombohedra, and is very difficultly soluble in water. Its hot solution appears to be stable.

## ANALYSIS.

	Calculated for $Cs_2BaFe(CN)_{11} \cdot 3H_2O$ .	Found.
Cesium.....	39.71	38.03
Barium.....	20.53	20.42
Iron.....	8.37	8.53
Water ....	8.07	8.01

Crystallography, rhombohedral.  $a:c = 1.515$ . Angle between basal plane and rhombohedron =  $119^\circ 45'$  (calculated). Rhombohedral angle =  $82^\circ 30'$ .

This salt adds confirmatory testimony to the amount of water of crystallization in barium potassium ferrocyanide, and also to the close crystallographical resemblance between the salts of the type  $M'BaM'''(CN)_{11} \cdot 3H_2O$ . ( $M' = K, Cs$ ;  $M''' = Fe, Ru, Os$ ).

## THE CAFFEIN COMPOUND IN KOLA. PART II. KOLATANNIN.<sup>1</sup>

BY JAMES W. T. KNOX AND ALBERT B. PRESCOTT.

THE investigation of the caffein compound in kola conducted by us last year<sup>2</sup> showed us that it was a kolatannate of caffein instead of a glucoside as formerly supposed. This question then arose: Is the tannin of this body identical with the free tannin existing in the kola nut? In the very brief examination made at that time it seemed that there was some difference, for combustions of both kinds of the tannin showed a difference in the respective amounts of carbon and hydrogen of each. No interpretation of the results was made at that time, for we considered the data insufficient, and the question was not settled.

It became necessary, in order that this point might be positively determined, to make a thorough comparative study of these two forms of kolatannin, and the research has been continued along this line with results which are stated in the following pages.

### CLASSIFICATION OF TANNINS.

Several different means of classifying tannins have been proposed, such as "physiological" and "pathological"—referring, of course, to their origin in the plant; glucosidal and non-glucosidal; "iron-blueing" and "iron-greening;" tannins which are tanning agents and those which are not; those which yield a trihydroxyphenol by sublimation or by fusion with potassium hydroxide, and those which yield a dihydroxyphenol by sublimation, or the salt of a dihydroxybenzoic acid by gentle fusion with potassium hydroxide.<sup>3</sup>

Trimble<sup>4</sup> suggests a classification, not as a final one but which answers very well for the present, in view of the still very defective knowledge of this class of bodies. He proposes a division of them into "the gall tannin group" and "the oak tannin group." The tannins of the gall tannin group contain 50 to 52.5 per cent. of carbon and 3.10 to 4.50 per cent. of hydrogen; those of the oak tannin group contain, in round numbers, sixty

<sup>1</sup> Presented by the Special Research Committee at the Forty-fifth Annual Meeting of the American Pharmaceutical Association, August, 1897.

<sup>2</sup> Knox and Prescott, 1896: *This Journal*, 19, 63.

<sup>3</sup> Prescott: *Organic Analysis*, p. 466.

<sup>4</sup> Trimble: *The Tannins*, II, p. 131.



per cent. carbon and five per cent. hydrogen. This classification holds good for the following reactions also :

	Gall tannin group.	Oak tannin group.
Ferric salts.	Blue color and precipitate	Green color and precipitate.
Calcium hydroxide	White precipitate becoming blue.	Light pink precipitate becoming red and then brown.
Bromine water.	No precipitate.	Yellow precipitate becoming brown.

Under this classification kolatannin is to be compared with the oak tannin group, for its compositions and reactions coincide more nearly with those of oak tannin than with those of gallo-tannic acid. We include herewith a brief summary of some important work done on oak bark tannins, not only for its historic interest, but because it has a bearing indirectly upon our own work on kolatannin.

#### RECENT LITERATURE OF OAK BARK TANNINS.

In February, 1880, Böttinger<sup>1</sup> published a lengthy article on "oak red," phlobaphene and tannin, which was followed about a month later by Etti's<sup>2</sup> publication of his own work on oak tannin—a valuable contribution to its literature. The methods used by them in the preparation of their working samples differed radically, the botanical source of their barks or extracts was unknown to them (or, if known, was not stated), the tannins obtained possessed properties different from each other, and it is not strange that the results obtained by these investigators were at variance in many particulars. If we may judge by their descriptions, it would seem that Etti's method of separation was much more likely to yield a pure product than that used by Böttinger, although by no means free from objections. Without doubt this work of Etti and that of Löwe,<sup>3</sup> dated in September of the same year, but which did not appear until the following year, added more to the knowledge of oak tannins than any previous contributions had done. The methods used by them are noteworthy, because they were radical departures from the old lead acetate methods formerly so much in vogue.

<sup>1</sup> C. Böttinger, 1880; *Ann. Chem.*, (Liebig), 202, 269.

<sup>2</sup> C. Etti, 1880; *Monatsh. Chem.*, 1, 262.

<sup>3</sup> J. Löwe, 1881; *Ztschr. anal. Chem.*, 20, 208.

Etti extracted the oak bark with very dilute alcohol under gentle heat and added acetic ether and ordinary ether to the extract. After agitating, the faintly red-colored ethereal layer was separated, the ether recovered by distillation and used again for the same purpose. After distilling the ether, the alcoholic solution of tannin remaining behind was found to contain some crystals of ellagic acid, which were removed by filtration and the filtrate evaporated to dryness on a water-bath. The residue, a reddish-white powder, was oak tannin, mixed with a little phlobaphene, amorphous resin and gallic acid; the two last-named substances were separated by extracting the powder with non-alcoholic ether; it was next treated with a mixture of three parts acetic ether and one part ethyl ether, which removed the tannin and left the phlobaphene undissolved. After distilling off the solvent, the pure tannin remained behind as a reddish-white powder. Etti insists, too, that if the ethyl acetate be used again for a solvent it must be washed with sodium hydroxide solution and redistilled before use, as the tannin tends to decompose it slightly into acetic acid and alcohol, while the tannin is itself partially converted into its anhydride.

The method of Böttinger depends on the separation of the phlobaphene from tannin solutions by means of its comparative insolubility in water. The tanbark is extracted first with ether, then with alcohol, the alcohol solution is evaporated to dryness, and the residue extracted again with ether which removes the last traces of wax and fat. By warming the residue with water on a water-bath, a partial separation is effected of the insoluble phlobaphene from the soluble tannin. After filtration the tannin solution, still containing traces of phlobaphene, is repeatedly evaporated and redissolved, until upon diluting the liquid very largely and cooling it, no precipitation is had. On evaporating this solution, a light-colored residue is obtained which is soluble in water and which he considered the pure tannin.

Löwe extracted the oak bark with ninety per cent. alcohol, and distilled the extract *in vacuo* to syrupy consistency. Water was then added, which precipitated a large quantity of anhydride; after filtration common salt was added to saturation, which precipitated the remaining anhydrides completely; the liquid, after filtration, was agitated with ether repeatedly until this sol-

vent would remove nothing further from the solution. The remaining ether was dissipated by gentle heat and after cooling the solution was shaken out with acetic ether. The acetic ether was removed by distillation and cold water was added to the remaining residue as long as precipitation ensued, after which it was again filtered and evaporated slowly in a vacuum desiccator to a dry mass, which is soluble in water and becomes cinnamon-brown on being pulverized.

It will be noticed that the methods of Etti and Löwe have much in common, the principal difference from the other methods being in the use of ethyl acetate, an immiscible solvent. It is difficult to say to whom credit should be given for the first application of this solvent to the preparation of tannin. In 1873,<sup>1</sup> however, Löwe mentions having used it in his work on sumach tannin, while in 1872<sup>2</sup> he also made use of it as a separative solvent for gallotannic acid.

Etti ascribed the formula  $C_{11}H_{16}O_8$  to his tannin: a "first anhydride"  $C_{11}H_{10}O_{11}$ , was formed by heating the tannin at  $140^{\circ}C$ . He separated a ready-formed anhydride from the bark corresponding to this one, and made use of its barium salt  $C_{11}H_{10}BaO_{11}$ , to determine its formula. By boiling it with dilute hydrochloric or sulphuric acid, it loses another molecule of water, forming a second anhydride  $C_{11}H_{10}O_{10}$ . The third anhydride he prepared by boiling the pure tannin with dilute mineral acid, whereby two molecules of tannin lost three molecules of water, forming a body to which he ascribed the formula  $C_{22}H_{18}O_{11}$ . This anhydride corresponds, in Etti's opinion, to Oser's oak-red. Boiling the pure tannin with potassium hydroxide solution for some time, formed the first anhydride identical with the so-called oak bark phlobaphene; this was separated by acidulating the alkaline solution with mineral acid and filtering out the precipitated anhydride.

By various experiments, such as boiling the tannin with dilute acids, digesting it with ferments, etc., he arrived at the conclusion that oak tannin was not a glucoside but that such evidence of glucose as had been found by other investigators was due to the accidental presence of glucose in the sample.

He proposed a structural formula, the same as that of digallic

<sup>1</sup> J. Löwe, 1873: *Ztschr. anal. Chem.*, 12, 128.

<sup>2</sup> J. Löwe, 1872: *Ztschr. anal. Chem.*, 11, 365.

acid with three hydroxyl groups replaced by three methyl groups, he having detected methyl chloride by burning the gas formed by heating the tannin with concentrated hydrochloric acid in a sealed tube.

Böttinger's work was principally on oak phlobaphene and oak-red, which he considered identical. The oak-red was formed by boiling the tannin with dilute mineral acid. He ascribed the formula  $(C_{14}H_{10}O_6)_3 \cdot H_2O$  to it and believed oak tannin to be a glucoside.

Löwe proposed the formula  $C_{42}H_{28}O_{14}$  for the tannin he prepared and  $C_{42}H_{28}Pb_2O_{14}$  for the lead salt. He also prepared oak-red by the usual process of boiling the tannin with dilute acids and obtained in addition to the oak-red,  $C_{42}H_{28}O_{14}$ , a by-product of which he made a combustion, but did not identify. It was not sugar, however, and he states that oak tannin does not conduct itself as a glucoside. The oak phlobaphene is, according to his statements, a fourth anhydride of oak tannin of the formula  $C_{42}H_{28}O_{14}$ , and forms a lead salt  $C_{42}H_{28}O_{14}Pb$ .

A somewhat extended and not altogether good-natured controversy between Böttinger and Etti followed the publication of the latter's paper, Böttinger<sup>1</sup> insisting upon the correctness of his own work, and holding to his first statement that oak tannin was a glucoside, Etti,<sup>2</sup> on the other hand, contended that Böttinger's methods were faulty, that ready-formed glucose would not be separated from the tannin by Böttinger's process, and therefore sugar would of course be found in the solution after boiling the tannin with dilute acids. He performed a number of experiments tending to prove the correctness of his position, following Böttinger's methods also and criticising him severely. Böttinger<sup>3</sup> subsequently modified his position somewhat, but without conceding anything of importance.

In 1883 the next contribution appeared, in which Etti<sup>4</sup> again commented on Böttinger's work and quoted Löwe in confirmation of his own results. He reported a new tannin, of formula  $C_{42}H_{28}O_{14}$ , from *Quercus Pubescens*, while the other he had since

<sup>1</sup> C. Böttinger, 1881: *Ber. d. chem. Ges.*, 14, 1598.

<sup>2</sup> C. Etti, 1881: *Ber. d. chem. Ges.*, 14, 1826.

<sup>3</sup> C. Böttinger, 1881: *Ber. d. chem. Ges.*, 14, 2390.

<sup>4</sup> C. Etti, 1883: *Monatshefte*, 4, 512.

learned was from *Quercus Robur*. This new tannin colored solutions of ferric salts green, while the first one produced a blue color with them. During this investigation the objection already noted to the use of ethyl acetate, *viz.*, its tendency to decompose the tannin, became so marked as to necessitate a different method of separation. The most important points of this new method are the use of alcoholic ether as a solvent for the tannin, phlobaphene and green resin. The resin is removed from the resulting product by benzene, and the phlobaphene by careful addition of lead acetate to the tannin solution. The precipitate of lead tannate is yellow, but if any anhydride (phlobaphene) be present, the precipitate will be colored more or less reddish-brown, depending on the proportion of it to the tannin. Lead acetate is added until the color of the precipitate indicates that all of the anhydride has been precipitated. After filtering, the liquid is again exhausted with alcoholic ether, the ether removed by distillation and the residual liquid evaporated to dryness on the water-bath. A rather remarkable peculiarity of Etti's work is that both of these tannins are nearly insoluble in water, 0.6 of tannin in 100 of water, while the experience of other workers has been quite generally that tannins are soluble.

Etti claimed to have formed four anhydrides of this tannin,  $C_{40}H_{30}O_8$ .

First anhydride,	$C_{40}H_{30}O_{17}$ .	Oak phlobaphene, dried at $120^{\circ}$ .
Second	" $C_{40}H_{30}O_{18}$ .	By boiling phlobaphene with 1 : 12 sulphuric acid and washing precipitate first with water, then with alcohol, and evaporating the alcoholic solution.
Third	" $C_{40}H_{34}O_{15}$ .	Dried at $125^{\circ}$ . By boiling tannin with dilute sulphuric acid and collecting the precipitate.
Fourth	" $C_{40}H_{32}O_{14}$ .	By heating in 25 per cent. sulphuric acid containing 20 per cent. alcohol in sealed tube at $130^{\circ}$ for four hours.

Etti believed also that four anhydrides were formed from the other tannin ( $C_{17}H_{10}O_8$ ) and gave this view support by his own figures and some also of Oser, of Böttinger and Löwe. This would be apt to mislead the casual reader into attaching more importance to this theory of the four anhydrides, than is war-

ranted by the actual results given by Etti. It would hardly seem that he was justified in making this use of the work of the other investigators. As a matter of fact he has selected figures here and there which gave support to his views, but ignored others of equal importance which did not harmonize with his ideas; *e. g.*, he quoted Löwe's figures for the analysis of oak-red, but did not mention his work with the lead salts of oak-red, which brought him to the conclusion that the formula of oak-red was  $C_{28}H_{22}O_{11}$ . There is no apparent reason for doubting that this work was equally as reliable as that which Etti quoted, and to omit it gives a careful reader the impression that deductions made from such peculiarly isolated facts would not necessarily be of great value. The chart is here appended:

	Calculated.	Found.		
Tannin..... } C <sub>17</sub> H <sub>16</sub> O <sub>9</sub> ..... }	Carbon..... 56.04 Hydrogen.. 4.40	56.31 4.63	56.06 4.69	
First anhydride ..... } "Phlobaphene," .... }	Carbon..... 57.46 Hydrogen.. 4.22	57.28 4.64	57.62 4.33	
C <sub>34</sub> H <sub>30</sub> O <sub>17</sub> ..... }				
Grabowski's oak-red. }				
Second anhydride ... } C <sub>34</sub> H <sub>28</sub> O <sub>16</sub> ..... }	Carbon .... 58.96 Hydrogen.. 4.04	58.76 4.20		
Third anhydride .... } C <sub>34</sub> H <sub>26</sub> O <sub>16</sub> ..... }	Carbon..... 60.58 Hydrogen .. 3.86	By Oser. 60.70 4.03	By Böttinger. 60.19 4.22	By Etti. 60.08 4.03
Oser's oak-red..... }				
Fourth anhydride ... } C <sub>34</sub> H <sub>24</sub> O <sub>14</sub> ..... }	Carbon..... 62.20 Hydrogen.. 3.66	Found by Löwe. 62.339 62.197 61.997 4.154 4.015 4.056		
Löwe's oak-red..... }				

Böttinger<sup>1</sup> published in the same year, 1883, a piece of work done on the bromine derivatives of oak tannin. By direct addition of bromine to the watery extract of oak bark he formed a dibrom oak tannin,  $C_{16}H_{14}Br_2O_{10}$ , which was capable of forming a pentacetyl derivative. "By careful manipulation"—he does not describe it—he converted the dibrom into a tetrabromtannin, which also formed a pentacetyl compound. This seems to be the first work on bromine derivatives.

In 1884<sup>2</sup> he investigated hemlock tannins by means of their

<sup>1</sup> C. Böttinger, 1883: *Ber. d. chem. Ges.*, 16, 2710.

<sup>2</sup> C. Böttinger, 1884: *Ber. d. chem. Ges.*, 7, 1041.

bromine compounds precipitated directly from their infusions by addition of bromine. Later<sup>1</sup> in the same year he prepared bromine compounds of a number of bark tannins by adding bromine directly to their infusions. Acetyl compounds of these were formed and analyzed.

Etti,<sup>2</sup> in a brief paper shortly afterward, discussed the points of difference between gallotannic acid and oak tannin. He also pointed out that by reason of its very hygroscopicity acetic anhydride was not a proper agent for determining the number of hydroxyl groups of tannins, as its tendency would be to form anhydrides which in turn would be acetylated and lead to incongruous results in the analysis.

Böttiger,<sup>3</sup> in 1887, published an article principally on oakwood tannin, which he separated by dissolving commercial oakwood extract in twenty parts of water and allowing it to stand. The clear liquid was evaporated to dryness and boiled with acetic anhydride, which formed an acetyl compound whose composition corresponded to formula  $C_{16}H_7(C_2H_3O)_6O_9$ . From this he recovered an anhydride of oakwood tannin and formed mono- and tetrabrom derivatives of it.

In 1889, Etti,<sup>4</sup> adhering to his previously published formulas for oak tannins, gave the results of an investigation of a tannin from the common Slavonian oak, to which he gave the formula  $C_{16}H_{14}O_9$ . It was nearly or quite insoluble in water. He formed several soluble magnesium salts with this tannin and suggested that it might exist in the plant in this form, thus accounting for its solubility in an aqueous menstruum when first extracted. Several anhydrides were formed.

Any résumé of the literature of oak tannins, however brief, would be incomplete without reference to the work of Trimble.<sup>5</sup> His monograph in two volumes contains a praiseworthy compilation of previous literature on the subject and full accounts of his own work. He has the credit of introducing acetone as an extractive menstruum for the oak tannins instead of alcohol. This solvent is said to act particularly well with oak bark. A

<sup>1</sup> C. Böttiger, 1884: *Ber. d. chem. Ges.*, 17, 1123.

<sup>2</sup> C. Etti, 1884: *Ibid.*, 17, 1820.

<sup>3</sup> C. Böttiger, 1887: *Ann. Chem.* (Liebig), 238, 366.

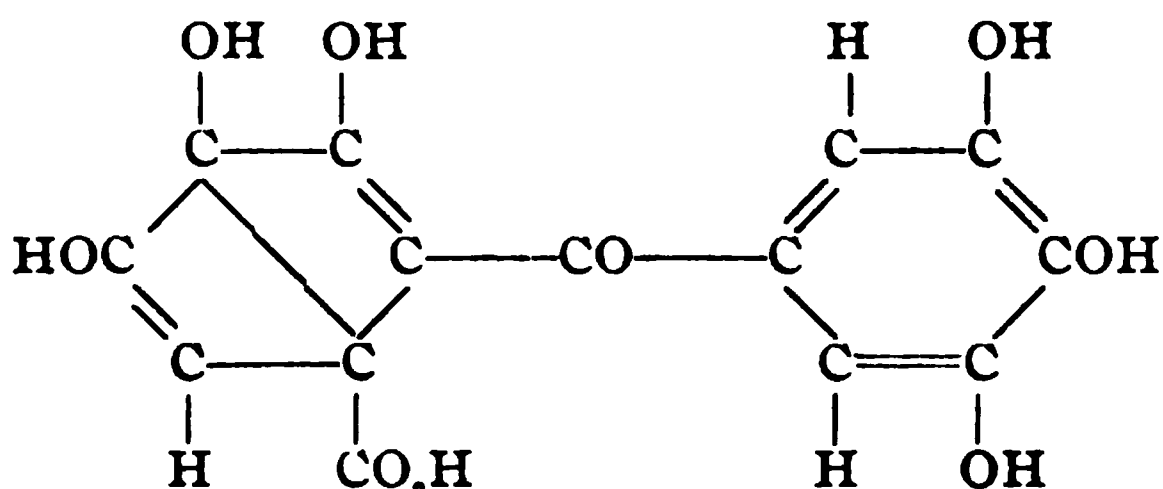
<sup>4</sup> C. Etti, 1889: *Monatshefte*, 10, 547.

<sup>5</sup> H. Trimble, 1894: "The Tannins." A monograph, J. B. Lippincott Co.

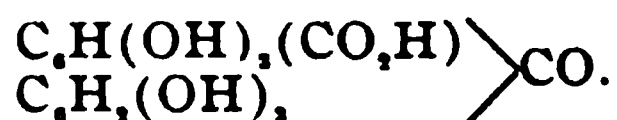
good bibliography concludes the work. He has confined himself thus far to analyses of the pure tannins and does not as yet propose formulas. In addition to the monograph just mentioned, he has been a frequent contributor on this subject in the periodical literature of chemistry.

#### LATE WORK OF SCHIFF ON DIGALLIC ACID.

In the present year, Hugo Schiff,<sup>1</sup> having already found that natural tannic acid is possessed of a slight optical activity, namely dextrorotatory, inquires as to its containing in some way asymmetric carbon, and infers a ketonic structure with six hydroxyl groups. He does not obtain a hydrazone from tannic acid. From experimental results he proposes this formula :



Irrespective of orientation, and for comparison of a kolatannin formula offered for consideration further on, the above formula may be held simply as



#### CAFFEOTANNIC AND CAFFEIC ACIDS.

The literature of caffeotannic acid, of the formula  $\text{C}_{18}\text{H}_{16}\text{O}_{11}$ , dates from Rochleder, in 1846.<sup>2</sup> Its production of caffeic acid (dihydroxyphenylacrylic acid), along with sugar, was set forth by Hlasiwetz in 1867.<sup>3</sup>

A few years ago, caffeic acid was obtained from the tannin of coffee, also from the tannin of the maté, by H. Kunz-Krause.<sup>4</sup> Very recently the same author has investigated caffeotannic

<sup>1</sup> *Gazz. chim. ital.*, 1897, 27, i, 90.

<sup>2</sup> *Ann. Chem. (Liebig)*, 59, 300.

<sup>3</sup> *Ibid.*, 142, 220.

<sup>4</sup> *Arch. Pharm.*, 1893, 231, 613.



acid.<sup>1</sup> In his report he<sup>2</sup> finds confirmation of the composition of caffeic acid as a dihydroxyphenylacrylic acid. His analyses obtain the carbon dioxide given off when the caffeic acid is heated to 200° C., and are confined to this analytic method. A residue of a vinyl pyrocatechol is predicted. The author recognizes a class of bodies which he terms glucotannoids.

### “FREE” KOLATANNIN.

#### PREPARATION OF THE SAMPLE.

The amorphous character of tannins, together with their extreme liability to decomposition, renders their separation and purification very difficult. The method used by us last year,<sup>3</sup> in the very brief examination of kolatannin, was based on that of Allen,<sup>4</sup> being fractional precipitation with lead acetate.

On taking up the work this year, it soon became evident that whatever may be said of lead-acetate methods as applied to other tannins, they certainly are unsuited to this one, for various reasons. The lead kolatannate, being bulky, is extremely slow and difficult of filtration, and the tannin in this state exhibits a marked tendency to pass into insoluble forms, principally anhydrides. During the washing, the lead salt becomes gradually darker, and this tendency is favored by the moisture present. If, on the other hand, the washing be less prolonged, the resulting product will be contaminated with various other constituents of kola extract, such as sugar, alkaloids, inorganic salts, coloring-matter, etc., etc. It is indeed very doubtful if any usual amount of washing will remove these impurities, hence the purity of a tannin, separated by precipitation with lead acetate, would be regarded with too much suspicion to be employed in analytical work, even if its sensible properties were not changed during the treatment. Kolatannin was at first supposed and since determined to be soluble in water. But on evaporating the solution of tannin after removing the lead from combination by hydrogen sulphide, the end-product was a red-brown

<sup>1</sup> I am indebted to Prof. Kremers for bringing Kunz-Krause's article in the July *Berichte* to my attention, as I read this paper in the August meeting of the American Pharmaceutical Association.—A. B. P.

<sup>2</sup> *Ber. d. chem. Ges.*, 1897, 1617.

<sup>3</sup> Knox and Prescott, *loc. cit.*

<sup>4</sup> Allen: *Com. Org. Anal.*, 3, pt. I., 76.

substance, insoluble in water, and possessing a not particularly astringent taste. So by the use of lead acetate a tannin is obtained whose purity is a matter of doubt, and whose properties have undergone radical changes during separation, both as to color and solubility. Furthermore, we desired to effect a perfect separation of the free tannin from that existing in combination with caffein (as caffein kolatannate) in order to determine by analysis whether they were identical tannins or not, the analysis of them last year having shown somewhat different values in each for carbon and hydrogen. Caffein kolatannate is sparingly soluble in water, more soluble in solutions of tannin and of caffein, so that the aqueous infusion of kola contains caffein kolatannate as well as free tannin, and the lead tannate obtained from it would be a mixture of the lead salts of both tannins, or both forms of tannin, and no delicate separation could be had in this way.

Plainly, another method was necessary. The objections just noted were for the most part neither new, nor limited to kola-tannin. As previously stated, Löwe, in 1872, who had encountered many difficulties in the use of lead acetate for the separation of tannins, and found it necessary to employ other means to obtain a pure product, resorted to the use of ethyl acetate. This immiscible solvent, proving satisfactory in many cases, has since been used considerably, either alone or mixed with ether, in the separation of tannins for analytical purposes, and for some tannins at any rate is unquestionably the best separative solvent which has yet been given publicity as such. At the same time a single shaking out with ethyl acetate does not suffice for the preparation of a pure sample. More or less coloring-matter will be found in the residue left on evaporating the first portion of the solvent, so that several repetitions of the process are required. Care must be used not to carry the method of purification too far, for if this be done the decomposition of the tannin is apt to prove a greater obstacle than the original impurities. We find that four or five repetitions of the "shaking out" give the best results. In detail the manipulations are as follows, and the method has given satisfactory results:

The fresh kola nuts are sliced into boiling alcohol,<sup>1</sup> removed after a few moments boiling, and dried in a current of warm air, then ground up to a number twenty powder and packed firmly in a percolator. The alcohol so used in sterilizing the drug is diluted to about fifty per cent. strength, and employed as a menstruum, with addition of sufficient dilute alcohol to complete the extraction. The highly-colored extract of kola thus obtained is concentrated by distillation *in vacuo*, until the alcohol is all removed. This can be done with a good pump at between 18° and 20° C. The contents of the flask are then filtered, the insoluble portion being chiefly caffein kolatannate, while the solution contains caffein, kolatannin, caffein kolatannate, glucose, traces of fatty matter, and more or less colored derivatives of tannin according to whether the sterilization by boiling alcohol has been properly done. Common salt is then added to this filtrate to saturation and the caffein kolatannate is completely precipitated. It is filtered out and added to the first residue of caffein kolatannate. The reddish-colored filtrate is then transferred to a large separatory funnel and agitated with chloroform repeatedly to remove alkaloids and traces of fat. The dissolved chloroform is then separated by agitation with small portions of ether. Kolatannin is insoluble in chloroform, and only very sparingly soluble in ether, so this treatment does not remove any considerable amount of it. Ethyl acetate is now added to the liquid in the separatory funnel and the liquid extracted with it as long as any tannin is removed. Usually eight, ten, or even more successive portions are required for this. The united solutions of tannin in ethyl acetate are transferred to a distilling flask and concentrated to dryness under reduced pressure. To avoid loss of the ethyl acetate we use a condenser about a meter in length, and pack the receiver in ice. Sometimes also a condenser is placed between the pump and the receiver. With these precautions the waste is very slight. Before using the recovered ethyl acetate as a solvent again, however, it is washed with a weak solution of sodium carbonate and redistilled, to avoid the presence of any free acetic acid formed by decomposition of the ether. The statement of Etti already alluded to, concern-

<sup>1</sup> To prevent the formation of the colored body, which would otherwise appear.

ing the decomposition of ethyl acetate by tannin, has not been found to apply to kolatannin, but the washing was nevertheless adopted as a precautionary measure.

The tannin residue in the distilling flask is a porous, pinkish mass, very friable, and easily and completely soluble in water. It is redissolved in a convenient quantity of saturated salt solution, filtered if need be and again shaken out with ethyl acetate, which is distilled off in the way just described. The tannin residue is next dissolved in cold distilled water and shaken out as before, this process being repeated once or twice. The final tannin residue, after the ethyl acetate has been removed as far as possible by distillation, is treated in the flask with a small quantity of ether, which after thoroughly permeating the mass is removed by distillation, using only the partial force of the pump and gentle heat. This is repeated several times until the mass has no odor of ethyl acetate. Then transferring to a vacuum desiccator the tannin is kept for several days over sulfuric acid. If this does not remove the last traces of ether, gentle heat ( $60^{\circ}$ – $65^{\circ}$ ) will do so.<sup>1</sup>

#### PROPERTIES OF KOLATANNIN.

Kolatannin is a cream-colored powder with a slight pinkish tinge. It is freely and completely soluble in water, alcohol, acetone, ethyl acetate, sparingly soluble in ether, insoluble in chloroform and in petroleum benzin. The following tabulated comparative statement of its reactions will serve to point out some of the important differences between it and gallotannic acid, and to indicate the close resemblance between this tannin and that of oak bark.

<sup>1</sup> We desire to take this means of expressing our appreciation of the liberality and courtesy of the firm of Frederick Stearns & Company, Manufacturing Pharmacists, Detroit, Michigan, who supplied us with a large quantity of True African Kola nuts, for our research this year. The drug was quite fresh and in perfect preservation, very necessary conditions for work of this kind.

REACTIONS OF TANNINS.

	Kolatannin. Free.	Kolatannin. From caffein kolatannate.	Oak tannin. (Trimble.)	Gallotannic acid.
Ferric acetate .....	Green.	Green.	Green.	Blue-black.
Potassium dichromate..	Dark brown ppt.	Dark brown ppt.	Brown ppt.	Brown ppt.
Chlorine .....	Pale ppt.	Pale ppt.		
Bromine ..	Light yellow ppt.	Light yellow ppt.	Yellow ppt.	No ppt.
Calcium hydroxide.....	Pink, then red, changing to ppt.	Pink, then red, changing to ppt.	Red, changing to ppt.	Darkens with bluish tinge, then ppt.
"Tartar Emetic" .....	No ppt.	No ppt.	White ppt.	White ppt.
Quinin ...				
Cinchonin }	White ppt.	White ppt.	Ppt.	White ppt.
Caffein... }				
Albumen.....	Ppt.	Ppt.	Ppt.	Ppt.
Lead acetate.....	White ppt.	White ppt.	White ppt.	White ppt.
Ammoniacal potassium ferricyanide .....	Deep red.	Deep red.	.....	Deep red.
Solution of formalde- hyde with a condens- ing agent, as HCl.....	Pink ppt., becoming red.	Pink ppt., becoming red.		

## COMBUSTIONS OF KOLATANNIN.

The tannin was analyzed by combustion with the following stated results :

	I.	II.	III.	Calculated for $C_{16}H_{16}O_8$ .
Carbon .....	56.74	56.81	56.90	56.45
Hydrogen .....	5.71	5.62	5.76	5.90
Oxygen .....	37.55	37.57	37.34	37.65
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

Having this satisfactory evidence of the preparation of a pure chemical compound, we next proceeded upon the task of determining its constitution, first by finding the number of hydroxyl groups in the molecule containing  $C_{16}$ .

## PENTACETYL KOLATANNIN.

An acetyl derivative was next formed for the object above stated. The tannin was boiled with acetyl chloride for about one hour under a return condenser, then an equal volume of glacial acetic acid was added, after which the liquid was poured slowly into ice-cold water. The acetyl compound separated out as a voluminous whitish precipitate. This was rapidly filtered at the pump and well washed with cold water, then it was dried with bibulous paper and finally in a vacuum desiccator over sulphuric acid. It was a nearly white or gray-white powder, tasteless, having a faint odor of acetic acid, and was insoluble in water, sparingly soluble in ether, and freely and completely soluble in chloroform, in alcohol, and in glacial acetic acid.

Analysis of the body gave the following stated results:

	By combustion.	I.	Found. II.	III.	Calculated for $C_{16}H_{16}(C_2H_3O)_5O_8$ .
Carbon .....		56.55	56.68	56.76	56.72
Hydrogen .....		5.39	5.36	5.24	5.47
Oxygen .....		38.06	37.96	38.00	37.81
By saponification.					
Acetyl .....		38.24	38.47	38.68	39.09

On comparing the values given by analysis with those calculated for the pentacetyl derivative, the agreement seems to be satisfactory.

The acetyl values in the analysis by saponification as detailed below are a little low, but it is quite possible that this is to be

ascribed to defects in the method of estimation rather than to other causes. At any rate the acetyl content seems without doubt to indicate five hydroxyl groups in the  $C_{11}$  molecule rather than four or six.

The analyses by combustion were made in the ordinary way: the estimation of acetyl was conducted in the manner next described.

#### DETERMINATION OF ACETYL.

The acetyl compound, one-half to one gram, varying with the supposed acetyl content, is boiled with thirty to forty cc. of six per cent. sulphuric acid in a flask fitted with reflux condenser, for two hours. 100 to 150 cc. water are now added and without filtration the volatile contents of the flask distilled into a known quantity of decinormal potassium hydroxide solution, being careful to avoid a high enough temperature or sufficient concentration to cause distillation of the sulphuric acid. More water is now added to the distilling flask and the distillation repeated. The contents of the receiver should be kept alkaline and a few drops of phenol-phthalein solution added, so that any change in the reaction of the solution may be instantly noted. The distillation should be repeated several times until the last one hundred cc. of distillate contains no acetic acid. The excess of alkali is to be titrated with decinormal hydrochloric acid, and the amount of acetic acid calculated from the difference between the amount of alkali solution first taken, and the quantity of hydrochloric acid required to neutralize it. Barium chloride is now added, and if any precipitation takes place, the barium sulphate is collected and weighed, the sulphuric acid calculated and correction made for it. If a halogen be present in the acetyl compound, a sufficient excess of silver sulphate is added to the contents of the distilling flask before distillation, to precipitate it completely as silver salt.

The above was occasionally deviated from by heating the acetyl compound with the dilute acid in sealed tubes two or three hours at  $130^{\circ}$ , then cooling, opening, transferring to a flask and distilling as before described.

The following described method was used a few times, but without apparent advantage over the others: The sample is

boiled with twenty times its weight of alcoholic solution of potassium hydroxide, of five to eight per cent. alkali strength, in a flask under return condenser. Phosphoric acid is added in excess and the contents of the flask distilled with steam into a receiver containing a known quantity of decinormal alkali solution. To drive the acetic acid over completely requires distillation of about a liter of water. The same precautions are observed as in the preceding methods if halogens are present.

### BROMINE DERIVATIVES OF KOLATANNIN.

The bromine compounds of this tannin have been investigated at considerable length, for the purpose of obtaining further data concerning its constitution.

#### TRIBROM KOLATANNIN.

When bromine water is added to a water solution of kolatannin, a dark-colored body is precipitated, and with continued addition of the reagent the precipitation goes on until complete, during which the precipitate formed becomes lighter-colored until at the end, in the presence of an excess of bromine, it is pale brownish-yellow and further addition of bromine water produces no change. It is quite voluminous and cannot well be filtered at the pump, but is collected by ordinary filtration and well washed with water until the washings remain clear when treated with silver nitrate solution. It is dried first on porous plates, then in a vacuum desiccator to constant weight.

During the process of drying it gradually changes color until it becomes reddish-brown. It is odorless and nearly tasteless, insoluble in water, ether, chloroform, and benzene, but is readily soluble in alcohol and in acetone.

In the clear filtrate, after the bromine compound has been removed, hydrobromic acid is easily identified, and for that reason the change is believed to be one of substitution. It may be questioned perhaps whether this is not caused by the action of bromine on the water; the bromine water, however, was freshly prepared, and the hydrobromic acid formed under these conditions would be very little. But in preparing twenty-five or thirty grams of this bromine compound, after its precipitation, the filtrate was agitated with carbon disulphide to remove the excess



of bromine, then separated and the aqueous portion concentrated to small volume, which had an acid taste and reaction and in which hydrobromic acid was easily identified.

The bromine compound was analyzed with the following stated results :

By combustion.	I.	Found. II.	III.	Calculated for $C_{16}H_{17}Br_3O_8$ .
Carbon . . . . .	32.91	33.12	....	33.28
Hydrogen . . . . .	2.69	2.58	....	2.95
Oxygen . . . . .	22.86	22.63	....	22.19
As silver salt.				
Bromine . . . . .	41.54	41.67	41.62	41.58

The percentage of carbon in this body, when compared with that of the pure tannin from which this was prepared, seemed to indicate the substitution of three hydrogen atoms by that number of bromine atoms.

#### PENTACETYL TRIBROM KOLATANNIN.

(From Tribrom Kolatannin.)

For the purpose of obtaining further data, an acetyl compound of the bromine derivative was formed : The bromine compound is boiled with acetyl chloride for about forty-five minutes, under a reflux condenser. An equal volume of glacial acetic acid is added to the clear red solution and the liquid well cooled by freezing-mixture. Then it is poured slowly into twelve or fifteen times its volume of ice-cold water, which is constantly stirred. A thermometer should be kept in the beaker containing the precipitate, and if the temperature rises above  $10^{\circ}$ , it is best to cool the contents by placing the beaker in a freezing-mixture, resuming addition of the acetyl chloride on cooling, until all has been used. The acetyl compound separates as a flocculent yellow precipitate, is quickly filtered, well washed and dried, first on porous plates, then in a vacuum desiccator.

It is a tasteless, golden-yellow powder, having a faint odor of acetic acid. It is insoluble in water, nearly insoluble in ether, but soluble in alcohol, in acetone, and in chloroform. It loses acetic acid when gently heated, and both bromine and acetic acid on stronger heating. It was analyzed with the following stated results :

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{12}Br_3(C_2H_2O)_2O_8$
Carbon .....	39.43	39.55	39.65
Hydrogen .....	3.44	3.34	3.44
Oxygen .....	26.57	26.65	26.43
As silver salt.			
Bromine .....	30.56	30.46	30.48
By saponification.			
Acetyl .....	26.91	27.12	27.32

The results obtained agree very closely with the calculated formula and give additional confirmation to the formulas assumed for the pure tannin and its tribrom compound.

#### HALOGEN DETERMINATION.

For the halogen determinations in the bromine compounds of kolatannin, the well-known process of heating the halogen derivative with fuming nitric acid and silver nitrate in a sealed tube for two hours at  $175^\circ$ , was followed. Experience taught us, however, to first make a preliminary determination with a considerable excess of silver nitrate to ascertain the approximate amount of halogen present. For example, where in one case the preliminary determination indicated 40.88 per cent. of bromine, the following ones, in triplicate with only a slight excess of silver nitrate, were respectively 41.54 per cent., 41.67 per cent., 41.62 per cent. And as a rule the preliminary determinations have given low results, but are necessary to furnish data for the second and more exact estimations.

Having learned the approximate amount of halogen present, the following details of manipulation were followed: The size of the sample taken is adjusted so that the weight of the resulting silver salt shall be 0.15 to 0.20 gram. Six or eight per cent. more than the theoretical quantity of silver nitrate is now weighed and placed with the sample in a hard glass tube with six cc. fuming nitric acid, after which the tube is sealed and heated at  $175^\circ$ – $180^\circ$  for two hours. It is then opened and the contents are transferred to a beaker with about 100 cc. water and heated on the water-bath for one-half hour. The silver bromide is then collected on weighed asbestos filters connected with the pump, washed successively with hot water, alcohol and ether, and dried twenty or thirty minutes at  $80^\circ$ – $85^\circ$  to constant weight.

In some cases the excess of silver nitrate in the filtrate was deter-

mined gravimetrically as silver chloride for a check on the results.

Our thanks are due to Professor Edward D. Campbell, of this University, for many valuable suggestions on halogen and acetyl determinations.

#### TRIBROM PENTACETYL KOLATANNIN.

(From Pentacetyl Kolatannin.)

Having acetylated the tribrom compound of tannin and obtained a pentacetyl derivative of it, we decided to brominate the pentacetyl compound and determine by analysis whether or not the resulting product was identical, in other words to ascertain whether the order in which the substitutions were made affected the result.

This bromination was accomplished by dissolving the pentacetyl tannin in strictly pure, anhydrous chloroform, free from alcohol, and adding a slight excess of bromine. The solvent was then distilled off in partial vacuum, while the brominated acetyl compound remained behind as a golden-yellow mass. This was treated with ether several times and redistilled, using the pump to remove the traces of chloroform, and finally transferred to a vacuum desiccator and left until completely dry.

In color, taste, and solubilities this body is identical with that obtained by acetylizing the tribrom derivative. It was analyzed with the following stated results:

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{18}Br_3(C_2H_3O)_5O_8$ .
Carbon.....	39.49	39.62	39.65
Hydrogen.....	3.39	3.47	3.44
Oxygen.....	26.61	26.34	26.43
As silver salt.			
Bromine .....	30.51	30.57	30.48
By saponification.			
Acetyl .....	26.84	26.98	27.32

Inasmuch as the results of the analysis of this body coincide quite as closely with the theoretical figures as in the preceding case, it may be safely assumed that the bodies are identical and that in the preparation of a pentacetyl tribrom kolatannin it makes no difference whether the bromine or acetyl is introduced first.

## TETRABROM KOLATANNIN.

We next wished to ascertain whether this tannin was capable of taking more than three bromine atoms into combination in each molecule. Nothing but the tribrom derivative was formed by treating an aqueous solution of the tannin with bromine water in excess, so another solvent was tried successfully. Taking a weighed quantity of tannin, it was dissolved in alcohol and bromine was added gradually to the alcoholic solution in slight excess of the theoretical quantity necessary to form a tetrabrom derivative. The liquid remained clear, all the bromine compounds of kolatannin that we have yet prepared being easily soluble in alcohol. The bromine compound was precipitated by pouring the brominated alcoholic solution into twelve or fifteen volumes of ice-cold water; being insoluble in water, it was separated as a voluminous reddish-brown precipitate, which was filtered, washed and dried in the way already described under the method of preparation of tribrom kolatannin.

This body agrees in solubilities with the tribrom compound; it is slightly darker, however, and has a faint odor of bromine. It was analyzed with the following stated results:

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{18}Br_4O_8$ .
Carbon.....	29.59	29.46	29.27
Hydrogen.....	2.46	2.38	2.44
Oxygen .....	18.97	18.88	19.52
As silver salts.			
Bromine .....	48.98	49.28	48.77

This, then, is a tetrabrom derivative of kolatannin. From it an acetyl compound was formed, following the manipulations already described.

## PENTACETYL TETRABROM KOLATANNIN.

This acetyl compound was yellow and but slightly darker than that of the tribrom derivative. In other physical properties it appeared identical with that body.

It was analyzed with the following stated results:

	Found.		Calculated for
By combustion.	I.	II.	$C_{16}H_{11}Br_4(C_2H_3O)_6O_8$
Carbon.....	35.82	35.97	36.03
Hydrogen.....	3.02	2.95	3.01
Oxygen .....	24.02	24.14	24.02
As silver salt.			
Bromine .....	37.14	36.94	36.94
By saponification.			
Acetyl .....	24.42	24.59	24.83

From the above it is seen that the tetrabrom derivative forms a pentacetyl compound equally as easily as the tribrom derivative.

#### PENTABROM KOLATANNIN.

This derivative was formed while trying to prepare a hexabrom substitution product, but by reason of an insufficiency of bromine the resulting product yielded analytical results corresponding fairly well with those calculated for pentabrom kolatannin.

	Found.		Calculated for
By combustion.	I.	II.	$C_{16}H_{11}Br_5O_8$
Carbon.....	25.87	25.99	26.13
Hydrogen ....	2.07	1.86	2.04
Oxygen.....	17.35	17.31	17.42
As silver salt.			
Bromine .....	54.71	54.84	54.41

This body may be a mixture of the hexa- and tetrabrom tannins. It is somewhat difficult of formation, however, and we have not always been able to obtain it in a manner analogous to the methods of preparation of the other bromine compounds. We do not consider that all conditions necessary to its formation are yet understood. There is no good evidence that this is a mixture of the other derivatives, however, and for the present there is really no sufficient reason for mentioning it as other than a pentabrom tannin. It is soluble in the same agents as the other bromine compounds, and is less stable than the tetrabrom compound, the odor of bromine being much more distinct. It appears to be characteristic of these bodies, that with increasing percentage of bromine, there is decreasing stability (that is to say, a greater tendency to lose bromine), and darker color.

## PENTACETYL PENTABROM KOLATANNIN.

(From Pentabrom Kolatannin.)

This was prepared by acetylizing pentabrom kolatannin in the usual way. In properties and appearance it closely resembles the other bromacetyl derivatives, except that its color is somewhat darker yellow. It was analyzed with the following stated results:

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{10}Br_5(C_2H_3O)_5O_8$ .
Carbon.....	33.54	33.39	33.02
Hydrogen.....	2.77	2.65	2.65
Oxygen.....	20.97	21.37	22.01
As silver salt.			
Bromine.....	42.72	42.59	42.32
By saponification.			
Acetyl.....	22.15	22.36	22.75

This body was also prepared from pentacetyl kolatannin, as stated next below.

## PENTABROM PENTACETYL KOLATANNIN.

(From Pentacetyl Kolatannin.)

Having ascertained by previous experiment that addition of a considerable excess of bromide to an alcoholic solution of kolatannin, resulted in the formation of a hexabrom derivative, we wished to prepare a hexabrom pentacetyl derivative by brominating the pentacetyl derivative in the same manner.

Analysis of the resulting product showed, however, that contrary to our expectations, not a hexabrom, but a pentabrom, derivative was formed, identical with the one described in the preceding section. The analytical results obtained were as follows:

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{10}Br_5(C_2H_3O)_5O_8$ .
Carbon.....	33.19	32.97	33.02
Hydrogen.....	2.60	2.71	2.65
Oxygen.....	21.90	21.95	22.01
By silver salt.			
Bromine.....	42.31	42.37	42.32
By saponification.			
Acetyl.....	22.31	22.47	22.75

## HEXABROM KOLATANNIN.

By treating an alcoholic solution of kolatannin with bromine

in considerable excess a hexabrom compound is formed, which is separated in the same way as the tetra- and pentabrom derivatives. It is darker colored than either of the others, has a very distinct odor of bromine, and is soluble in the same media as the other bromine compounds. It was analyzed with results stated next below :

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{10}Br_6O_8$ .
Carbon .....	23.48	23.57	23.59
Hydrogen .....	1.68	1.79	1.72
Oxygen .....	15.73	15.38	15.73
As silver salt.			
Bromine .....	59.11	59.26	58.96

#### TETRACETYL HEXABROM KOLATANNIN.

(From Hexabrom Kolatannin).

This acetyl compound was prepared in the usual way, by boiling with acetyl chloride and was supposed, before analysis, to be a pentacetyl derivative. It had a dark yellow color, a faintly pungent taste and a slight odor of bromine and acetic acid. Soluble in chloroform and in alcohol, insoluble in water. The analytical results which are next stated show it to be a tetracetyl hexabrom tannin :

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{10}Br_6(C_2H_3O)_4O_8$ .
Carbon .....	29.57	29.39	29.33
Hydrogen .....	2.21	2.32	2.25
Oxygen .....	19.41	19.21	19.55
As silver salt.			
Bromine .....	48.81	49.08	48.87
By saponification.			
Acetyl .....	16.86	17.19	17.52

#### INDICATIONS OF MOLECULAR CONSTITUTION.

From the analytical results of the pentacetyl pentabrom tannin and of the hexabrom compound with its tetracetyl derivative, it appears that the total number of groups or atoms which may be substituted in the way described is ten ; that if five of acetyl be introduced first, only five bromine atoms may be substituted for hydrogen, but that if the bromine be introduced first six bromine atoms can be introduced by carrying bromination to the limit, and in this hexabrom compound only four hydroxyl

groups remain. This appears to indicate that the sixth bromine atom introduced bears a relation to the molecule in some respect different from that of any other bromine atom. But it might be expected that a limit would be reached in the total number of negative groups or atoms which can be retained in the molecule. The greatest number of acetyl groups probably indicates the entire number of hydroxyls. And a balance of evidence seems to favor the conclusion that there are six atoms of hydrogen directly united with the carbon of a benzene chain. These numbers are all in ratio to sixteen atoms of carbon. That the molecule contains  $C_{16}$ , or some multiple of this, appears from the quantitative results. We attempted to find the molecular weight of kolatannin, tribrom kolatannin and pentacetyl tribrom kolatannin by the cryoscopic method, but the results so far obtained are utterly meaningless. Further indications of molecular constitution may be drawn from a study of the anhydrides, account of which next follows, also from the results of the action of acids, and especially from the products by fusion with alkali, all stated further on in this paper.

### THE ANHYDRIDES OF KOLATANNIN AND THEIR DERIVATIVES.

By judiciously heating kolatannin several anhydrides may be prepared, as described below, the amounts of water driven off varying with the temperature and the duration of its application. The first anhydride of the series, that in which two molecules of tannin lose one molecule of water, and whose empirical formula is  $(C_{16}H_{10}O_7)_2O$  is formed by heating kolatannin at  $107^{\circ}$ – $110^{\circ}$  to constant weight. This anhydride is darker colored than the tannin from which it is prepared and is less soluble in water. The second anhydride, by an oversight, we did not attempt to prepare. If we may judge by the temperature required for the preparation of the first, third and fourth members of the series, this one would result from heating the tannin a sufficient time at  $120^{\circ}$ – $125^{\circ}$ . Its theoretical formula is  $C_{16}H_{10}O_7$ . The third anhydride,  $(C_{16}H_{10}O_7)_3O$ , results from heating the tannin at  $135^{\circ}$ – $140^{\circ}$ . It is dark reddish-brown and nearly or quite insoluble in water. The fourth anhydride,  $C_{16}H_{10}O_7$ , is



dark brown, insoluble in water, and is the result of heating kolatannin two hours at  $155^{\circ}$ – $160^{\circ}$ .

These anhydrides are all soluble in alcohol, and in solution of kolatannin of sufficient concentration.

#### FIRST ANHYDRIDE.

The method of preparation has been described in the preceding section. This is a yellowish-red body, soluble in water, in alcohol, and in dilute alkali solutions. The calculated loss of weight of the tannin in preparing this anhydride was 2.65 per cent. The observed loss of weight was 2.77 per cent. The body was subjected to combustion with the following stated results:

	Found.		Calculated for ( $C_{18}H_{18}O_7$ ) <sub>2</sub> O.
	I.	II.	
Carbon.....	58.27	58.39	58.18
Hydrogen.....	5.38	5.61	5.45
Oxygen .....	36.35	36.00	36.37

#### FIRST ANHYDRIDE OF TRIBROM KOLATANNIN.

The first anhydride of kolatannin was dissolved in water and precipitated by adding an excess of bromine, collecting the precipitate by filtration, and drying exactly as described in the method of preparation of tribrom kolatannin. It is soluble in the same media as tribrom kolatannin, is darker colored, is odorless and tasteless. Analysis of it proved to be an anhydride of tribrom kolatannin.

	Found.		Calculated for ( $C_{18}H_{18}Br_3O_7$ ) <sub>2</sub> O.
By combustion.	I.	II.	
Carbon.....	33.61	33.80	33.86
Hydrogen.....	2.92	2.76	2.65
Oxygen .....	21.31	21.17	21.16
As silver salt.			
Bromine .....	42.16	42.27	42.33

#### FIRST ANHYDRIDE OF TETRABROM KOLATANNIN.

Prepared in the same way as tetrabrom kolatannin, using in this case the first anhydride of kolatannin. It is hardly to be distinguished from the other tetrabrom compounds in appearance or other sensible properties. It was analyzed with the following stated results:

By combustion.	I.	Found. II.	Calculated for (C <sub>16</sub> H <sub>18</sub> Br <sub>4</sub> O <sub>7</sub> ) <sub>2</sub> O.
Carbon .....	29.47	29.66	29.72
Hydrogen.....	2.37	2.21	2.17
Oxygen.....	18.57	18.42	18.58
As silver salt.			
Bromine .....	49.59	49.71	49.53

## FIRST ANHYDRIDE OF HEXABROM KOLATANNIN.

This was prepared by adding a considerable excess of bromine to the alcoholic solution of the first anhydride of kolatannin, and separating the product in the usual way. It is dark red, tasteless, and has a faint odor of bromine; is insoluble in water, ether, and chloroform; soluble in alcohol and in dilute alkali solutions. It was analyzed with the following stated results:

By combustion.	I.	Found. II.	Calculated for (C <sub>16</sub> H <sub>18</sub> Br <sub>6</sub> O <sub>7</sub> ) <sub>2</sub> O.
Carbon.....	23.96	24.15	23.88
Hydrogen.....	1.64	1.69	1.49
Oxygen .....	14.61	14.57	14.93
As silver salt.			
Bromine .....	59.79	59.59	59.70

## THIRD ANHYDRIDE OF KOLATANNIN.

The method of preparation has been described. The calculated loss of weight on heating the tannin was 7.96 per cent.; the observed loss was 8.16 per cent. It is a red-brown powder, odorless, nearly tasteless, but somewhat astringent. Soluble in alcohol and in alkali solutions, insoluble in water, ether, and chloroform. It was analyzed with the following stated results:

By combustion.	I.	Found. II.	Calculated for (C <sub>16</sub> H <sub>17</sub> O <sub>6</sub> ) <sub>2</sub> O.
Carbon .....	61.72	61.80	61.54
Hydrogen .....	5.29	5.46	5.13
Oxygen .....	32.99	32.74	33.33

The bromine derivative of this anhydride and those of the fourth anhydride to be described further on in these pages, were prepared in a manner strictly analogous to those already described.

## THIRD ANHYDRIDE OF TETRABROM KOLATANNIN.

A dark-brown, tasteless powder having a faint odor of bromine.

Insoluble in water, ether, or chloroform ; soluble in alcohol and in alkali solutions. The analytical results were :

By combustion.	Found.		Calculated for (C <sub>18</sub> H <sub>12</sub> Br <sub>4</sub> O <sub>4</sub> ) <sub>2</sub> O.
	I.	II.	
Carbon .....	30.59	30.73	30.57
Hydrogen.....	1.99	1.81	1.91
Oxygen.....	16.32	16.19	16.56
As silver salt.			
Bromine.....	51.10	51.27	50.96

THIRD ANHYDRIDE OF HEXABROM KOLATANNIN.

A dark-brown, tasteless powder having a distinct odor of bromine. It is insoluble in water, ether, and chloroform ; soluble in alcohol and in alkali solutions.

The analytical results were :

By combustion.	Found.		Calculated for (C <sub>18</sub> H <sub>11</sub> Br <sub>6</sub> O <sub>4</sub> ) <sub>2</sub> O.
	I.	II.	
Carbon .....	24.04	24.39	24.43
Hydrogen.....	1.52	1.38	1.27
Oxygen.....	13.22	12.88	13.23
As silver salt.			
Bromine .....	61.22	61.35	61.07

FOURTH ANHYDRIDE OF KOLATANNIN.

This was prepared in the way previously described. The calculated loss of weight attendant upon its preparation from kolatannin is 10.61 per cent. The observed loss is 10.78 per cent. It is a dark-brown, odorless, tasteless powder, soluble in alcohol and in alkali solutions ; insoluble in water, in ether, and in chloroform. It was analyzed with the following stated results :

	Found.		Calculated for C <sub>18</sub> H <sub>10</sub> O <sub>4</sub> .
	I.	II.	
Carbon .....	63.20	62.98	63.37
Hydrogen.....	5.09	5.16	4.95
Oxygen.....	31.71	31.86	31.68

FOURTH ANHYDRIDE OF TETRABROM KOLATANNIN.

A dark-brown, tasteless powder having a faint odor of bromine. Soluble in alcohol and in alkali solutions ; insoluble in water, in ether, and in chloroform. It was analyzed with the following stated results :

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{12}Br_4O_8$ .
Carbon .....	30.91	30.68	31.02
Hydrogen.....	1.95	1.86	1.78
Oxygen.....	15.40	15.58	15.51
As silver salt.			
Bromine .....	51.74	51.88	51.69

#### FOURTH ANHYDRIDE OF HEXABROM KOLATANNIN.

A very dark-brown powder having a distinct odor of bromine. Soluble in the same media as the previously described bromine compounds. The analytical results are :

	Found.		Calculated for
By combustion.	I.	II.	$C_{18}H_{12}Br_6O_8$ .
Carbon.....	24.96	24.79	24.71
Hydrogen.....	1.39	1.21	1.16
Oxygen.....	11.70	12.01	12.35
As silver salt.			
Bromine .....	61.95	61.89	61.78

#### PRODUCTS OF THE ACTION OF DILUTE ACIDS UPON KOLATANNIN.

When kolatannin is boiled with dilute sulphuric or dilute hydrochloric acid, it first passes into solution, and on continued boiling a reddish precipitate is formed, which becomes gradually darker the longer the heating is kept up. This precipitate is collected by filtration and well washed with water, in which it is insoluble. It is also insoluble in alcohol, and only partially soluble in alkali solution. Combustions of this substance, while giving fair duplicates for the same sample, indicate that its composition is not uniform and constant. Samples Nos. I and IV were prepared by boiling kolatannin with six percent. sulphuric acid, in a flask fitted with a return condenser ; No. II by heating the tannin and dilute acid in a sealed tube ; No. III by boiling the tannin and dilute acid in a beaker with occasional addition of water to compensate for evaporation ; No. V by boiling caffein tannate with dilute acid in a flask fitted with return condenser ; No. VI is the result of combustion of a similar substance made and reported last year.<sup>1</sup>

	I.	II.	III.	IV.	V.	VI.
	Av. of 2.	Av. of 2.	Av. of 2.	Av. of 2.	Av. of 2.	Av. of 2.
Carbon ...	53.60	50.45	51.27	56.38	54.49	69.20
Hydrogen.	5.34	4.85	5.24	5.69	5.87	6.70
Oxygen...	41.06	44.70	43.49	37.93	39.64	24.10

<sup>1</sup> Knox and Prescott, 1896: This Journal, 19, 89.

The aqueous filtrate was shaken out with ether, the residue after evaporation of the ethereal solution was redissolved in water and boiled a short time, which caused precipitation of the coloring-matter. Then filtering, it was again extracted with ether, and the operation repeated several times. At length the ethereal solution left a nearly colorless residue on evaporation, which responded to the tests for protocatechuic acid. Oak bark tannin also, when subjected to similar treatment with dilute mineral acids, yields protocatechuic acid.

Etti, Böttinger, and Löwe each mention the insoluble red body formed from oak tannin on boiling it with dilute acids and consider it an anhydride. They do not agree on which of the anhydrides it is, however. In fact, as already mentioned, there are many points in their work on tannins on which they were at variance. Etti<sup>1</sup> found gallic acid in the acid filtrate. Löwe<sup>2</sup> does not mention having examined the liquid for bodies other than sugar. Trimble,<sup>3</sup> however, whose work is the most recent, found protocatechuic acid as a by-product, in every case. He does not commit himself on the question of whether the dark brown, amorphous, insoluble substance, separated from tannin by the action of hot dilute acids, is an anhydride.

Whatever may be the relation of the body separated in this way from oak bark tannin to the original tannin, there does not as yet seem to us to be any good reason for considering the corresponding substance precipitated from acid solutions of kolatannin, an anhydride of kolatannin. The evidence thus far is against it. Boiling with dilute mineral acids is in general a means of hydrolysis, rather than anhydrolysis; we would therefore expect saponification instead of anhydride formation; as a matter of fact an aromatic acid—protocatechuic—has been found in the acid filtrate after collecting the insoluble red substance in question, while if the reaction were one of simple anhydride formation, no by-product should be present. If the red-brown substance were an anhydride of kolatannin, we would expect it to have a higher percentage of carbon than the original tannin, but in most cases combustion indicates a lower percentage of

<sup>1</sup> C. Etti, 1884: *Ber. d. chem. Ges.*, 17, 1820.

<sup>2</sup> J. Löwe, 1881: *Ztschr. anal. Chem.*, 20, 208.

<sup>3</sup> H. Trimble: "The Tannins," II, p. 92.

carbon. We would also expect to find the body of uniform composition when prepared by similar means, but the analyses just mentioned show that it is very variable in content of carbon and hydrogen, while its appearance also varies from red to dark brown. At present no more can be said of this body than we have already said; *viz.*, that it is red or dark brown, amorphous, insoluble in water, in alcohol, in ether and in chloroform, only partially soluble in dilute alkali, and that it is a decomposition product obtained by boiling kolatannin, or caffein kolatannate, with dilute mineral acids.

Knebel's<sup>1</sup> "kolaroth" is a body obtained in the same way, except that he prepared it from caffein kolatannate, or as he supposed "kolanin," which was the alleged "caffeine-bearing glucoside" of kola. Inasmuch as the free tannin of kola and that combined with caffeine are identical, as will appear further on in these pages, it makes no difference which kind of it is used for this purpose. Knebel, however, worked with caffeine tannate from the dried drug, while our work has been entirely on that from the fresh drug. He fails to give the figures of his combustion, but Hilger<sup>2</sup> reports the following stated results:

	Found.		Calculated for $C_{14}H_{12}(OH)_8$ .
	I.	II.	
Carbon .....	63.09	62.65	63.16
Hydrogen.....	6.85	6.50	6.75
Oxygen.....	30.06	30.85	30.09

This calculated formula does not differ widely in carbon content from that calculated for the fourth anhydride of kolatannin,  $C_{14}H_{10}O_8$ .

	Calculated for $C_{14}H_{10}O_8$ .
Carbon.....	63.37
Hydrogen .....	4.95
Oxygen .....	31.68

The hydrogen is rather high, however, which makes the oxygen correspondingly low. The results of an analysis of a body like the one Hilger analyzed might have been construed to indicate it as a member of the anhydride series, and inasmuch as he found a substance yielding analytical figures nearly coinci-

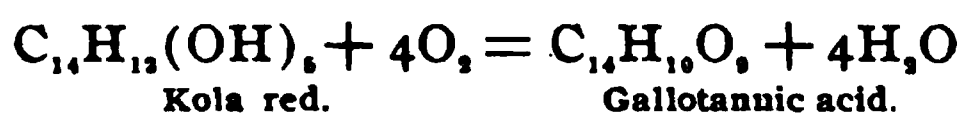
<sup>1</sup> E. Knebel, 1892: *Apoth. Ztg.*, 7, 112.

<sup>2</sup> A. Hilger, 1893: *Vierteljahr. f. öffentl. Gesundheitsg.*, 25, 559.

ding with those just given for the fourth anhydride, it is perfectly reasonable to suppose that if we had made combustions of a larger number of samples, we might have obtained some results which could be used in support of the idea that these decomposition products of tannins are simple anhydrides of them. Our experience has taught us that the composition of this product is by no means constant with the means used in its preparation, and we saw no good reason for selecting the figures of one combustion from those of a dozen others presumably as near correct, merely to give support to a theory.

It is somewhat puzzling that Knebel and Hilger have found this body of uniform composition. As a matter of fact Knebel reports no figures in support of his claim, and Hilger reports only two combustions; still it would be supposed that before assigning a formula to a body of this kind a larger number of combustions would have been made, and with different samples. We do not feel justified in accepting the formula  $C_{14}H_{12}(OH)_6$ , proposed by them for it, nor do we at present possess sufficient data for a formula. We do not even know that it is not a mixture of two or more substances; and although we have not made any separation of them, it seems to us more probable than otherwise that it is a mixture in varying proportions of certain products of decomposition of kolatannin.

The suggestion of Knebel that the tannin of kola is an oxidation product of "kolaroth" according to the equation



is untenable for the two-fold reason that we do not find kolatannin or this decomposition product of it to be so readily oxidizable as stated by him, and furthermore, the kolatannin is not identical with gallotannic acid, the formula of which he has given in the above equation as the formula of kolatannin, nor have we at any time found any gallotannic acid present in kola.

Knebel claims to have prepared a pure product of his kolaroth from the acetyl compound of it; and he further claims that the exact separation of kolaroth may be had by boiling his so-called "kolanin" (caffein kolatannate) with acetyl chloride, whereby an acetyl compound of "kola red" is formed, and is separated

by pouring the mixture of acetylchloride and caffein kolatannate into water. The acetyl compound of kola red is thus precipitated and the glucose and caffein pass into solution.

Let us examine this statement in the light of the recent knowledge of the chemistry of this interesting drug. First, as conclusively proven by us last year, the body called "kolanin" is not glucoside composed of caffein, glucose and "kola red," but is a combination of caffein with the tannin of kola,  $C_{12}H_{10}O_6$ , and with anhydrides of that tannin, in varying proportions, depending largely on the method used to separate it from the drug. And it contains no glucose whatever, for we have since learned that the evidence of sugar found in it, and in free kolatannin last year, and reported in our paper, was due to the accidental presence of glucose from a faulty method of separation. Moreover, acetyl chloride does not effect an exact separation of the caffein from this combination. We prepared an acetyl derivative of caffein kolatannate exactly as done with the other acetyl products and analyzed it, with the following results :

Carbon.....	58.30
Hydrogen.....	4.85
Nitrogen .....	2.54
Oxygen .....	34.31

The nitrogen content corresponds to 8.79 per cent. of caffein. The caffein kolatannate from which this acetyl compound was made contained 6.53 per cent. nitrogen, corresponding to 22.6 per cent. caffein. Caffein was also found in the liquid from which the acetyl compound was filtered. The separation then is not complete and the acetyl compound is not a pure acetyl compound of caffein kolatannate, nor was it expected to be ; for as caffein kolatannate contains kolatannin and some of its anhydrides, both capable of forming acetyl compounds, it naturally follows that any acetyl derivative prepared will not be a simple derivative of one of the bodies, as stated by Knebel, but will be a mixture of acetyl derivatives of the tannin and its anhydrides, probably in the proportions in which they existed prior to the operation. With this understanding of it, it is difficult to see how Knebel could have prepared the pure and simple acetyl compound in the way stated by him.



## THE QUESTION OF SUGAR PRODUCTION.

Results were obtained in our work last year which seemed to indicate that kolatannin was a glucosidal body. We wished to investigate this question more fully, and have done so in the following described way:

Kolatannin was dissolved in water and precipitated by lead acetate, and the collected lead salt washed with water for several hours; the lead salt was then decomposed by dilute sulphuric acid, the lead sulphate filtered out, and the acid filtrate boiled for four hours in a flask fitted with a return condenser. The acid strength was supposed to be about five to six per cent. The insoluble matter was filtered out, the acid removed by addition of barium carbonate, and the liquid again filtered; the coloring-matter was precipitated by lead acetate and the precipitate removed by filtration, after which the remaining lead acetate was removed by hydrogen sulphide. The filtrate was boiled to remove all the hydrogen sulphide, and made alkaline with a little sodium hydroxide solution. The liquid was still slightly colored. It was tested with Fehling's solution, and gave a red precipitate. A portion of it, made slightly acid with acetic acid, gave negative results when the osazone test was applied, and a control test made at the same time, using a little solution of grape sugar in addition, gave the well-known yellow precipitate. This showed that there was no interference with the phenylhydrazin test. Basic lead acetate solution was added, which precipitated the traces of coloring-matter in the solution, and, after removing the excess of lead, the solution was tested with Fehling's solution again, with negative results this time.

This experiment was repeated in a slightly different way, as follows: The well-washed lead salt of about one gram kolatannin was heated for two hours at  $110^{\circ}$  C. in a sealed tube with thirty cc. hydrochloric acid, the tube then opened and the contents filtered to remove lead chloride and the amorphous red decomposition product of kolatannin. The filtrate was red-colored and was shaken out several times with ether. The ethereal solutions were set aside for further examination. The filtrate was then boiled to remove the traces of ether, and exactly neutralized with sodium hydroxide, after which basic lead

acetate solution was added until no further precipitation occurred, the precipitate removed by filtration, and the excess of lead salt precipitated as lead sulphate by cautious addition of dilute sulphuric acid. The solution was again filtered, made slightly alkaline with sodium hydroxide solution, and tested with Fehling's solution with negative results.

The importance of using basic lead acetate to precipitate the coloring is shown by the fact that if only normal acetate be used a small amount of coloring-matter is left in solution and gives a precipitate with Fehling's solution, while if basic lead acetate be employed, all the coloring-matter is removed and the copper solution is not affected.

In the ethereal solution, protocatechuic acid in small quantity was found, as stated in another part of this paper.

The experiments described having given negative results, the interpretation is made that kolatannin is not a glucoside and that the evidence we had to the contrary last year was caused by the incomplete removal of the glucose of the plant, due to a faulty method of separation for the tannin, since discarded by us.

It is significant that this result places kolatannin in a category and gives it a character essentially different from the character of caffeotannic acid, as understood by the chemical world from the report of Hlasiwetz.

#### ACTION OF FUSED ALKALI.

Fifteen grams kolatannin were fused for two hours with potassium hydroxide, the fused mass cooled and acidulated with sulphuric acid, after dissolving it in water. Without filtering the mixture, it was shaken out with ether, the successive portions of this solvent united and evaporated. The residue was distinctly crystalline, the crystals assuming an arborescent form for the most part. This residue was purified several times by recrystallization, after which it was dissolved in water and submitted to tests. Protocatechuic acid and phloroglucin were found to be present.

#### ACTION OF HEATED GLYCERINE.

One gram kolatannin was heated with three cc. glycerine in a porcelain capsule for twenty minutes at 195°–200°. Fifty cc.

water were then added and the mixture was shaken out with ether. The residue left on evaporating the ethereal extract was found to contain protocathechuic acid, by chemical tests.

#### KOLATANNIN FROM CAFFEIN KOLATANNATE.

It has thus far not been found practicable to substitute other means of separation of this tannin from its caffein salt for the treatment by lead hydroxide, although the disadvantages of this agent are fully appreciated. It is, however, much to be preferred to lead acetate in this particular case, as lead acetate precipitates some caffein tannate along with the lead tannate, and the resulting tannin is apt to be contaminated accordingly.

#### PREPARATION OF THE SAMPLE.

The caffein tannate is dried on porous plates and finely powdered and sifted; it is then washed with a mixture of ether and chloroform to remove any traces of adhering fat, and dried again. It is then washed with ice-cold water by agitation, drained and washed again until the washings give no precipitate of silver chloride on being treated with solution of silver nitrate acidulated with nitric acid. The caffein kolatannate is now dissolved in dilute alcohol, making a very concentrated solution; this solution is filtered and poured into ten or twelve times its volume of ice-cold water, whereupon the caffein compound is reprecipitated. It is collected by filtration, drained well and redissolved in dilute alcohol, using gentle heat on the water-bath. Freshly precipitated lead hydroxide triturated to a smooth paste with warm alcohol is now added in excess and the mixture warmed on the water-bath for a few minutes, with stirring. The precipitate is now allowed to subside, and if sufficient lead hydroxide has been added the supernatant liquid will be colorless or faintly straw-colored, while the precipitate of lead kolatannate mixed with lead hydroxide forms a compact magma at the bottom of the container. The liquid, which contains kola alkaloids, is poured off and the precipitate is washed repeatedly with dilute alcohol, first by decantation and then by filtration, until several cc. of the filtrate evaporated in a porcelain dish leave no perceptible residue and give no test for caffein. The precipitate is compact and is much more readily washed than that given by lead acetate. It is then

suspended in dilute alcohol and treated with hydrogen sulphide until the tannin is all liberated. The lead sulphide is then filtered out and washed with dilute alcohol until the washings are colorless. The filtrate is concentrated by distillation *in vacuo* to small volume, and eight or ten volumes of water are added. This precipitates a reddish mass, a mixture of certain anhydrides of kolatannin, which is filtered out and set aside. The filtrate containing tannin together with dissolved anhydrides is now shaken with ether once or twice, and the washings thrown away. Then ethyl acetate is added and the tannin separated and purified in the way already described, under the method of preparation of kolatannin.

This "combined" kolatannin, although not quite as light-colored as the "free" tannin, shares all its reactions and solubilities.

#### COMBUSTION OF "COMBINED" KOLATANNIN.

It was analyzed by combustion and the following results obtained, which coincide very closely with those resulting from combustion of the "free" tannin:

	I.	Found. II.	III.	Calculated for $C_{16}H_{20}O_8$ .
Carbon.....	56.53	56.78	56.42	56.45
Hydrogen.....	5.68	5.79	5.74	5.90
Oxygen.....	37.79	37.43	37.84	37.65

#### THE PENTACETYL COMPOUND.

This was prepared in the same manner as the other acetyl derivatives and is identical with the pentacetyl compound of "free" kolatannin, heretofore described.

The analytical results are as follows:

	I.	Found. II.	III.	Calculated for $C_{16}H_{18}(C_2H_3O)_5O_8$ .
By combustion.				
Carbon.....	56.75	56.44	56.61	56.72
Hydrogen.....	5.54	5.41	5.31	5.47
Oxygen.....	37.71	38.15	38.08	37.81
By saponification.				
Acetyl.....	38.27	38.53	38.68	39.09

#### THE BROMINE COMPOUNDS.

These were prepared in identically the same way as the corresponding ones of the free tannin. In appearance and properties there seems to be no difference between these and those of

free kolatannin, and for the sake of brevity we shall omit further description and confine ourselves merely to the statement of analytical results in each case.

### TRIBROM DERIVATIVE.

By combustion.	I.	Found. II.	III.	Calculated for $C_{18}H_{17}Br_3O_8$ .
Carbon .....	33.09	33.25	....	33.28
Hydrogen .....	2.84	2.98	....	2.95
Oxygen .....	22.50	22.13	....	22.19
As silver salt.				
Bromine .....	41.57	41.64	41.74	41.58

### PENTACETYL TRIBROM DERIVATIVE.

(Formed by acetylizing the tribrom derivative.)

By combustion.	I.	Found. II.	III.	Calculated for $C_{18}H_{13}Br_3(C_2H_3O)_5O_8$ .
Carbon .....	39.64	39.82	....	39.65
Hydrogen .....	3.47	3.61	....	3.44
Oxygen .....	26.44	25.94	....	26.43
As silver salt.				
Bromine .....	30.45	30.63	30.71	30.48
By saponification.				
Acetyl .....	26.66	26.97	....	27.32

### TRIBROM PENTACETYL DERIVATIVE.

(Formed by brominating the pentacetyl derivative.)

By combustion.	I.	Found. II.	III.	Calculated for $C_{18}H_{13}Br_3(C_2H_3O)_5O_8$ .
Carbon .....	39.88	40.15	....	39.65
Hydrogen .....	3.26	3.45	....	3.44
Oxygen .....	26.34	25.74	....	26.43
As silver salt.				
Bromine .....	30.52	30.66	30.57	30.48
By saponification.				
Acetyl .....	26.78	27.04	....	27.32

### TETRABROM DERIVATIVE.

By combustion.	I.	Found. II.	Calculated for $C_{18}H_{16}Br_4O_8$ .
Carbon .....	29.13	29.35	29.27
Hydrogen .....	2.29	2.46	2.44
Oxygen .....	19.86	19.30	19.52
As silver salt.			
Bromine .....	48.72	48.89	48.77

## PENTACETYL TETRABROM DERIVATIVE.

By combustion.	I.	Found.	II.	Calculated for $C_{18}H_{11}Br_4(C_2H_3O)_6O_8$ .
Carbon.....	36.12		36.33	36.03
Hydrogen.....	2.78		2.96	3.01
Oxygen .....	24.33		23.78	24.02
As silver salt.				
Bromine .....	36.77		36.93	36.94
By saponification.				
Acetyl .....	24.64		24.78	24.83

## PENTABROM PENTACETYL DERIVATIVE.

(Formed by brominating the pentacetyl derivative.)

By combustion.	I.	Found.	II.	Calculated for $C_{18}H_{10}Br_5(C_2H_3O)_5O_8$ .
Carbon.....	33.23		32.98	33.02
Hydrogen.....	2.62		2.72	2.65
Oxygen .....	21.71		21.78	22.01
As silver salt.				
Bromine .....	42.44		42.52	42.32
By saponification.				
Acetyl .....	22.49		22.26	22.75

## HEXABROM DERIVATIVE.

By combustion.	I.	Found.	II.	Calculated for $C_{18}H_{14}Br_6O_8$ .
Carbon.....	23.85		23.68	23.59
Hydrogen.....	1.77		1.83	1.72
Oxygen .....	14.76		14.72	15.73
As silver salt.				
Bromine .....	59.62		59.77	58.96

## TETRACETYL HEXABROM DERIVATIVE.

By combustion.	I.	Found.	II.	Calculated for $C_{18}H_{10}Br_6(C_2H_3O)_4O_8$ .
Carbon .....	29.66		29.92	29.33
Hydrogen.....	2.46		2.29	2.25
Oxygen .....	18.73		18.55	19.55
As silver salt.				
Bromine .....	49.15		49.24	48.87
By saponification.				
Acetyl .....	16.48		16.73	17.52

KOLATANNIN ANHYDRIDES OBTAINED FROM CAFFEIN  
KOLATANNATE.

The insoluble, reddish-brown precipitate, formed on addition of cold water to the tannin solution after the separation of the tannin from its lead salt, as mentioned in the method of prepa-

ration of "combined" kolatannin, was well washed and dried at 100°. Combustion of this showed a carbon percentage intermediate between that of the second and third anhydrides of kolatannin.

As the solubilities of the anhydrides appear to be about the same, we were unable to effect a separation of them, and for this reason we heated the (supposed) mixture at 135°–140° to constant weight, in order to convert it all if possible into the third anhydride. It was then subjected to another combustion with the following results:

	I.	Found.	II.	Calculated for (C <sub>16</sub> H <sub>17</sub> O <sub>6</sub> ) <sub>2</sub> O.
Carbon .....	61.27		61.46	61.54
Hydrogen.....	5.28		5.43	5.13
Oxygen.....	33.45		33.11	33.33

These results agree very well with the calculated formula and with those obtained by combustion of the third anhydride of so-called "free" tannin of kola.

The identity of the tannin of caffein tannate with the free tannin having been positively settled by the analyses already given, and by one or two evidences yet to be stated, it was deemed unnecessary to make a further comparative study of its bromine derivatives.

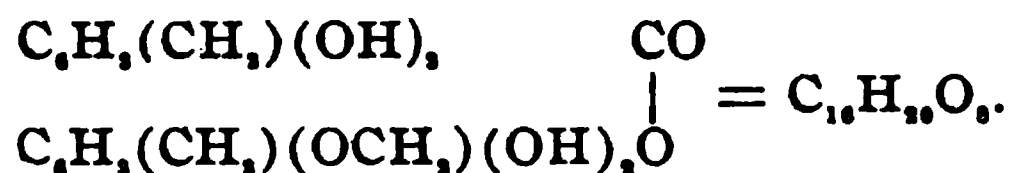
#### ACTION OF DILUTE ACIDS.

The experiments described as having been performed on "free" kolatannin, were repeated on this kind of kolatannin also with parallel results. The same is to be said of the products of fusion with potassium hydroxide and of heating with glycerine.

#### FURTHER INDICATION OF MOLECULAR CONSTITUTION.

Whether there be a carboxyl in kolatannin or not, remains open to question and to further determinations. Its moderate acid character is not inconsistent with the negative polarity of a polyhydric phenol, reinforced by the oxygen of an anhydride group, yet destitute of entire carboxyl. Our numerous analyses of kolatannin and its several derivatives as described in this paper, are in close agreement with a polyhydric phenol anhydride carrying two methyl groups and one methoxy group, but

standing altogether as a di-addition benzene derivative, two such benzene nuclei pairing together in an ester-like anhydride. On this supposition, a monomethyl dihydrogen trihydroxybenzoic acid has paired ester-wise with a monomethyl methoxydihydrogen trivalent phenol. The di-additive benzene constitution is not improbable among plant constituents of this class, finding parallel in the additive structure of the terpenes. If we admit the hypothesis of the molecular formula above indicated, we must predicate that one of the six hydrogen atoms joined to benzene-carbon is in position somewhat unfavorable to its bromine substitution, and when brominated quite preventing the acetylation of one of the hydroxyls. Finally, there remains no proof as to the distribution of the hydroxyl and methoxyl groups between the two benzene nuclei.



#### AS TO CHEMICAL BEARINGS UPON PHARMACOLOGY.

Finally, it must be admitted that the stable caffein compound of an acid of such marked chemical individuality as that of kola-tannin can by no means be assumed to have the same physiological effects as free caffein. And this subject is one of pharmacological importance for the caffein of all the beverage plants.

We are under many obligations to Mr. James Heggie, B.S., for his very efficient assistance in preparing and analyzing the various derivatives of tannin reported in the preceding pages.

#### DISCUSSION OF RECENT ASSAY METHODS.

Within the past year two processes for the assay of kola have been offered, which seem to us not to be free from objections. We give below the essential points of these methods without entering into unimportant details.

##### METHOD OF JEAN.<sup>1</sup>

The author ascribes his plan of procedure in part to MM. Chodat and Chuit. He boils the dried and powdered drug with "milk of lime," dries the whole in an oven and powders it again. This powder is exhausted with chloroform, which

<sup>1</sup> J. Jean, 1896: *Repert. de Pharm.*, (3), 7, 49.



removes the free alkaloids. The chloroform is evaporated to dryness, the residue dissolved in hot water and filtered. The filtrate is evaporated to dryness and weighed as caffein.

For "kolanin:" the drug, after treatment with chloroform, is extracted with alcohol, the alcohol evaporated from the percolate and the soft extract remaining is dissolved in boiling water, which solution, after cooling, is filtered. The insoluble matter remaining on the filter is dried in an oven and weighed as "kolanin."

The most serious defects in the above-described method are (1) the boiling with "milk of lime," (2) the prolonged heating necessary to dry the drug after that treatment, (3) weighing the caffein instead of estimating it with Wagner's reagent volumetrically, (4) the means employed to separate so-called "kolanin," (5) estimating caffein kolatannate ("kolanin") by weight as such, instead of by its caffein content.

(1) Boiling with "milk of lime," or other aqueous alkalies, tends to decompose caffein—a fact too well known to require further comment. This treatment also tends to liberate caffein from its tannate, and thus prevents an exact determination of the proportion of "free" to "combined" alkaloid that originally existed in the drug. The starch of kola, amounting to nearly forty per cent.,<sup>1</sup> causes the drug to become of a jelly-like consistence when boiled with aqueous liquids, and when dried the mass is very hard to powder, and even when powdered the condition of it is well calculated to resist the penetrating action of the solvent, and thus cause incomplete extraction.

(2) The gelatinous condition of the drug after boiling with "lime water" renders it hard to dry completely, and as very prolonged heating is necessary, there is danger of loss of caffein by sublimation.

(3) We do not consider that the alkaloids of kola are sufficiently pure when removed in this, the usual manner, to be weighed as such; Gomberg's<sup>2</sup> volumetric method gives more accurate results.

(4) If any caffein kolatannate escapes decomposition during the first part of the assay, which will occasionally happen, it is

<sup>1</sup> Knox and Schlotterbeck, 1895: *Proc. Am. Pharm. Assoc.*, 334.

<sup>2</sup> M. Gomberg, 1896: *This Journal*, 18, 331.

removed by the extraction with alcohol. But as it is somewhat soluble in water and more soluble in aqueous solutions containing tannin, the directions to collect and weigh the portion left undissolved by water will generally be found superfluous, for the small amount of it present will generally pass into and remain in solution. Dieterich<sup>1</sup> had this experience, and met with nothing but disappointment in trying to estimate caffein kولاتannate by this method.

(5) Caffein kولاتannate has been shown to be a body of somewhat variable composition, with a caffein content ranging from nineteen to twenty-five per cent. Inasmuch as the value of kola as a stimulant probably depends primarily on its percentage of caffein, and as the weight of its caffein compound indicates only approximately the amount of its combined caffein, there would not seem to be any reason for attaching much importance to the weight of this compound, if a very precise valuation of the drug is desired. We hold that a direct estimation of the caffein of this compound is preferable and at least as expeditious.

#### METHOD OF CARLES.<sup>2</sup>

Ten grams kola, one gram calcium hydroxide, and twenty grams eighty per cent. alcohol, are mixed together and dried on the water-bath until the weight is reduced to fourteen grams. The mixture is then powdered and transferred to a 100 cc. flask containing thirty-five cc. of a mixture of 100 parts chloroform and twenty parts alcohol, and heated one hour on a water-bath. After filtration the residue is extracted next with twenty cc. of the same solvent, and finally with ten cc. The united extracts are evaporated to dryness, and the residue taken up with ten cc. boiling water containing four or five drops of one per cent. sulphuric acid, then with six cc., and finally with five cc. The solutions are united, filtered, evaporated to constant weight, and weighed as caffein.

For "kolanin," which the author recognizes as caffein kولاتannate, another sample of the drug is taken and extracted with water to remove the caffein and other soluble constituents. The drug is next extracted with seventy per cent. alcohol, the extract evaporated to dryness, transferred to a filter, washed

<sup>1</sup> Dieterich, 1896: *Chem. Centrbl.*, 2, 675.

<sup>2</sup> P. Carles, 1896: *J. Pharm. Chim.*, 16, 104.

with cold water, then dried at gentle heat and weighed. If it be desired to estimate the alkaloids of this compound, one gram "kolanin," one gram calcium hydroxide, and three grams chalk with a little seventy per cent. alcohol are mixed together and evaporated on the water-bath to about six grams, and extracted with alcoholic chloroform in the manner already described.

The objections to this method are in part among those already mentioned in the discussion of Jean's method. The use of lime or other alkalies in the assay of a caffein-bearing drug is to be deprecated. The solvent used is not a proper one for the reason that sufficient alcohol is present to extract other constituents in addition to the alkaloids, which are not removed from the caffein during the subsequent treatment of the residue, and which, when weighed with the caffein, lead to erroneous results. Moreover, the manner of applying the menstruum is inconvenient, does not insure complete extraction, and is in no way preferable to the ordinary extraction by the use of Soxhlet's apparatus. The addition of the sulphuric acid is unnecessary and does not add to the purity of the final product, which is dark-colored and very plainly impure. The objection to weighing a final residue as caffein, finds especial application in this method.

As the properties of caffein kolatannate had not been made known very generally at the time of publication of these methods, there is some excuse for the assumption of both these writers that it is wholly insoluble. Carles has proceeded on this hypothesis in directing the drug to be extracted with cold water to remove the water-soluble constituents before exhausting it with alcohol to remove the caffein compound, but inasmuch as caffein kolatannate is not only somewhat soluble in water, but considerably more soluble in solutions of caffein and of tannin, the extraction of kola by water will remove a considerable amount of it. The same is to be said of the final washing of the caffein compound with water, which is quite inadmissible in quantitative work. Carles seems to have recognized the uncertain value of gravimetric determinations of caffein kolatannate, and is to be commended for offering an alternate method providing for its valuation according to the amount of its alkaloids.

At our request, Mr. James W. Cobb, Ph.C., has assayed a

sample of dried kola by each of the foregoing methods and by the method adopted by us last year,<sup>1</sup> after thoroughly familiarizing himself with them by preliminary work.

	Method of Jean.		Method of Carles.		Knox and Prescott.	
	I.	II.	I.	II.	I.	II.
Caffein by weight.....	1.93	1.79	2.16	2.33	....	....
The same titrated .....	1.83	1.71	1.87	1.98	1.96	1.88
"Kolanin" .....	none	none	2.89	3.17	....	....
Combined alkaloids... ..	....	....	....	....	1.62	1.61
Alkaloids of "kolanin" ....	....	....	0.59	0.69	....	....
Total alkaloids...	1.83	1.71	2.46	2.67	3.58	3.49

It will be seen that the impurity of caffein separated by Jean's method amounts to 4.84 per cent., and that of the caffein by Carles' method amounts to 14.25 per cent., which was determined by titrating the caffein with Wagner's reagent, after Gomberg's method.

Both give very low results as compared with those obtained by our own. They are tedious and otherwise unsatisfactory, in addition.

Further notes on the assay of kola are in preparation.

All the work reported upon in this paper has been done under the provision of the Stearns Fellowship of the University of Michigan.

ANN ARBOR, MICH., AUGUST, 1897.

## NOTE.

*A Correction.*—In the September number of this Journal the author, together with Mr. F. Thompson, published an article entitled "A Preliminary Thermochemical Study of Iron and Steel," in which they give the results obtained on a number of samples of iron and steel of different composition and which had been subjected to varying heat treatments. On taking up the work again this fall and reviewing critically the results of last year's work, I find that there are at least two serious errors in the results that I wish to explain now in order to prevent anyone else from being misled by the conclusions drawn from the results as stated in the article. The statement that the loss by radia-

<sup>1</sup> Knox and Prescott, 1896: This Journal, 19, 73.

tion was only  $0.24^\circ$  in one hour was a mistake of observation. Careful determinations on this point, made recently, show that it must have been  $1.24^\circ$  instead of the former figure. The error from not taking into account the loss by radiation will amount to from about fifteen to forty calories per gram of metal, the loss depending on the time of solution. Another source of uncertainty, and one for which the author alone is responsible, is the fact that the solution used for dissolving the samples contained about four per cent. of free hydrochloric acid, and consequently the solution of the iron may not in all cases have proceeded according to the equation,  $\text{Fe} + \text{CuCl}_2 = \text{FeCl}_2 + \text{Cu}$ , and this copper redissolved according to the equation  $\text{Cu} + \text{CuCl}_2 = \text{Cu}_2\text{Cl}_2$ . Part of the iron may have dissolved directly in the free hydrochloric acid, and, since the heat absorbed in the decomposition of  $2\text{HCl}$  is less than that necessary for the reduction of  $2\text{CuCl}_2$  to  $\text{Cu}_2\text{Cl}_2$ , more heat would be rendered sensible when a good deal of iron was dissolved directly in hydrochloric acid than when solution was effected through cuprous chloride.

The work is being gone over again very carefully with view to eliminating any errors that may exist in the previous work, and I therefore request that judgment be suspended on the previous work until further results may enable us to form a more reliable conclusion than could be drawn from our former data.

E. D. CAMPBELL.

ANN ARBOR, MICH., DECEMBER 14, 1897.

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### ERRATUM.

On page 942, line 5 (Vol. 19), for "antimony" read "phosphorus."

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### BOOKS RECEIVED.

A Practical Treatise on Mineral Oils and their By-Products, including a Short History of the Scotch Shale Oil Industry, the Geological and Geographical Distribution of Scotch Shales, Recovery of Acid and Soda used in Oil Refining and a List of Patents Relating to Apparatus and Processes for Obtaining and Refining Mineral Oils. By Iltyd I. Redwood. London: E. & F. N. Spon, Limited. New York: Spon & Chamberlain. 1897. xiv + 336 pp. Price \$6.00.

The Early History of Chlorine. Alembic Club Reprints, No. 13. Papers by Carl Wilhelm Scheele (1774), C. L. Berthollet (1785), Guyton de

Morveau (1787), and J. L. Gay-Lussac and L. J. Thenard (1809). Edinburgh: William F. Clay, 1897. 48 pp. Cloth. Price 1s. 6d.

Researches on the Molecular Asymmetry of Natural Organic Products. Alembic Club Reprints, No. 14. By Louis Pasteur, membre de la Société Chimique de Paris (1860). Edinburgh: William F. Clay. 1897. 46 pp. Cloth. Price 1s. 6d.

Ornithology of North Carolina. A List of the Birds of North Carolina, with Notes of Each Species. Issued by The North Carolina Agricultural Experiment Station, Raleigh, N. C. October 30, 1897. 36 pp.

Current Thought. New Series. Vol. 1, No. 1. January, 1898. C. Elton Blanchard, 802 Ansel Ave., Cleveland, Ohio. 21 pp.

The Mechanics of Soil Moisture. By Lyman J. Briggs, Physicist of the Division of Soils. Bulletin No. 10. U. S. Department of Agriculture, Division of Soils, Washington, D. C. 24 pp.

Second Report on Food Products. Twenty-first Annual Report of the Connecticut Agricultural Experiment Station for 1897. Part I. New Haven: The Tuttle, Morehouse and Taylor Press. 1897. xvi + 64 pp.

Montana Swine Feeding. Bulletin No. 14. Montana Agricultural Experiment Station, Bozeman, Montana. April, 1897. 36 pp. 4 half-tone plates.

# THE JOURNAL

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## AMERICAN CHEMICAL SOCIETY.

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### THE DIGNITY OF ANALYTICAL WORK.<sup>1</sup>

By C. B. DUDLEY.

**I**T will doubtless be conceded by all, that in the choice of the field to which one proposes to devote his life-work, a number of things should be consulted. Among these may be mentioned not only mental capacity and the opportunities for training by courses of study, which may be available to him, but also what may be termed natural inclination or love for the work. Just how much weight should be given to each of these elements, is a query not easily answered, but few will deny that genuine interest in or real love for the field of work chosen, should be allowed as great sway as possible. Those of us who have gotten far enough along in our life-work, to be able to look back somewhat, and to see and differentiate the causes that have shaped our line of effort, know full well that circumstances beyond our control, rather than our inclinations and desires, have in many cases determined our course, but the fact nevertheless remains, that for the best results, for the attainment of even moderate success, one's efforts must be in a field agreeable to him, and his heart must be in his work. Fortunate is the man for whom circumstances so shape themselves, that he is able to pass his years in the field of his choice, and spend and be spent in work that is congenial to him.

<sup>1</sup> Presidential Address delivered at the Washington Meeting of the American Chemical Society, December 29, 1897.

Assuming now that for most of us, circumstances and conditions have been such that we are spending our lives in the field of our choice, let us consider for a moment, a tendency that seems to be a concomitant of those thus fortunately situated. Do we not occasionally find in ourselves a disposition to magnify the importance of the field in which we happen to be engaged? Are we not somewhat inclined, quite naturally perhaps, to think that our field of work is more important than that in which others are occupied? Does not the theoretical chemist, whose inclinations lead him to spend his time in writing reactions, and building structural formulæ of wondrous architecture, often feel within himself, that his work is on a higher and nobler plane than that of the patient analyst, who has furnished the data which he uses? Does not the organic chemist who delights in the study of the carbon compounds, who can repeat for you series after series of chemical bodies, differing from each other by the constant addition of an element or group of elements, in whose vocabulary "types," "substitutions," "replacements," "condensations" and "isomers," are familiar words, and who, when a new organic compound is discovered, cannot rest until he has found to what series, and what place in the series, it belongs, or what its relations are to other bodies in that marvelous structure, based on the element carbon, which the studies of the last half century have reared before our eyes, I say does not this organic chemist oftentimes feel that he is engaged in a field far more worthy of study, and to which is due much more consideration, than to that of his inorganic brother, who devotes days and perhaps weeks to unraveling the constitution of some obstinate silicate, whose crystalline form gives little help, and whose oxygen ratio is hidden or obscure? Or again, does not the physical chemist oftentimes think, that with the tools of his more especial field, with his specific heats, his vapor-densities, his heats of chemical combination, and his ionic products, he is quite competent to solve all problems worth solving in the realm of chemistry, and that those who are engaged in other lines, are far below his standard, and can be looked down upon quite with pitying sympathy? Still once more, do we not often see the pure chemist whose battle cry is "original work for the work's own sake," claim for himself the highest



seat in the synagogue, and refuse to join his efforts with those of others whom he regards as his humbler brethren, *viz.*, those working in the field of applied chemistry, in securing the benefits of organization to extend and widen the borders of our science? Finally, not to make distinctions, do we not frequently see the analyst who knows so well how necessary it is to have the trained and skilful hand, and the acute and watchful brain, both working together, and at the same time, in order to secure the accuracy, without which his work is worthless, claiming for his field, that it is the foundation upon which our science rests, and that those who spend their time in locating the position of an atom in its molecule, or in finding the relations of an organic compound to other members of its series, or perchance in inventing long names for new compounds in which all the resources of the ancient Greek and Latin are brought to bear, to reveal in one word the constitution of the compound, I say does not the analytical chemist often regard these workers, as shallow, empty headed, and unworthy to be called chemists?

Now far be it from me to say that this partiality of each for his own field is blameworthy. We can, indeed, conceive of cases in which this partiality may be carried a little too far, but within proper limits, not only is it not blameworthy, but even as it seems to us, it may be praiseworthy for one to magnify the importance of the work in which he is engaged. A just and proper estimate of the value of his own work, a reasonable pride in his chosen science, or in that paddock of his science which it has fallen to the share of each to care for and cultivate, and indeed a moderate, though necessarily a somewhat partial, comparison of himself and his field of labor, with others, even though that comparison is somewhat to the detriment of the others, are not always necessarily bad. On the other hand, such pride and such comparisons tend to stimulate to renewed activity, tend to sustain in the perplexities and discouragements of work, and tend to keep one's effort concentrated on the work which he can do best. Looked at in this light, the generous rivalry of one branch of our science with another, or the pardonable pride of each in his own chosen field, and even in his own work, may be a distinct advantage, and I know you will bear with me a few minutes, while I, with proper modesty, and in

the true spirit, I hope, try to magnify a little, the field of analytical work.

To my mind, then, it is just and proper to take pride in analytical chemistry, because of the power which a properly conceived and executed analysis has of explaining difficulties. A few illustrations will, perhaps, make this point clear, and I am sure I will be pardoned for giving illustrations from my own experience, rather than historical ones.

Some years ago, after a passenger coach on the Pennsylvania Railroad had been through the hands of the car cleaners, it was noticed by some of the officers, that the paint on the outside looked very badly, and had apparently been injured by the cleaning. A careful examination by the paint experts revealed the fact that the varnish was nearly all gone, and in some places the paint itself partially removed. As a matter of discipline, the car cleaners were called to account, and requested to explain why the paint and varnish had been so badly injured. Their reply was that with the soap that was furnished for car cleaning no better results could be obtained. This statement was, of course, received with a grain of allowance, it being well known to railroad operating officers, that almost universally when anything goes wrong, and the men are called to an account, the materials are blamed. However, in order to give the men the benefit of the doubt, a sample of the soap was obtained, and submitted to analysis, when it was found that this soap actually contained over three per cent. of free caustic soda, and about seven per cent. of sodium carbonate. It is evident that this soap had been very carelessly made from cheap materials, and since it is well known that water solutions of both caustic and carbonated alkalis are fairly good solvents for dried linseed oil and other constituents of paint and varnish, it is clear that the defence of the men, in this case at least, was legitimate, and that the soap was really at fault. It may be added for information, that the circumstances above described led to the preparation of a specification for common soap, in which the amount of free and carbonated alkali was limited to very low figures, and that no similar difficulty of destruction of paint and varnish has since occurred.

Another illustration from a different field will emphasize the

power of an analysis to explain difficulties. A lot of boiler-plate was at one time received at Altoona shops, from one of the best makers. In this lot of forty or fifty sheets, two were found which gave difficulty in flanging, this operation consisting, as is well known, in bending over the edges of the sheets while hot, nearly at right angles to the balance of the sheet, in order to enable it to be joined to other sheets in the boiler. The two sheets referred to, cracked in the bend, although the remainder of the lot gave no difficulty from this cause. The workmen being thoroughly experienced, and the practices of the shop being excellent, the cause of the failure in the case of these two sheets, was not apparent. An analysis of samples from each of these sheets, however, showed 0.35 per cent., and 0.36 per cent. of carbon respectively, while analyses of samples from other sheets in the same lot showed in no case above 0.12 to 0.15 per cent. of carbon. The explanation of the difficulty seemed now quite clear. The shops had been supplied for a long time with the softer grade of steel, and the methods and practices in use were those applicable to that kind of steel. No wonder then that with the harder grade, difficulty should arise, as actually happened, and but for the analysis this might have passed into shop traditions as one of those unexplained and unexplainable crochets of steel, which both the makers and practical users of this metal delight in constantly bringing forward.

A single illustration further will, perhaps, suffice on this head. A few years ago, a shipment of some three hundred freight axles was received at two different shops on the Pennsylvania Railroad, from an entirely reputable maker. Some of these axles were used for repairs, and some went under new cars. Scarcely had they gotten into service, however, before difficulty began to arise. The axles began to break. Indeed, one of them broke before the car had been turned out of the shop yard, one broke into three pieces before the car had made 150 miles, and in less than three months eight had broken. Each of the broken axles was sent to the laboratory, and a careful study of the case made, with the hope of discovering the cause of the failure. An examination of the freshly fractured ends of several of the broken axles, showed that for a little distance in from the circumference, the fractured steel presented an appearance quite different from

that given by the remainder of the fracture. Moreover, a line of demarcation between these two apparently different kinds of steel in the same axle, could be clearly traced. Accordingly, it was decided to make analyses of borings from near the circumference and near the center, and see whether this would reveal anything. It may be stated that the axles were known to have been made from Bessemer steel, and should normally have contained not more than 0.10 per cent. of phosphorus. The analysis of the borings from near the circumference of the axles in no case gave figures up to this limit, while the borings from the center of the axles in no case showed less than 0.16 per cent. phosphorus, and in some cases the amount was as high as 0.24 per cent. Those who are familiar with the methods in daily use in modern steel works, will from these figures at once understand the cause of breakage of these axles. For the benefit of those who are not, it may be well to explain that in most modern steel works, large ingots are now the rule, and that in large ingots which take considerable time to solidify from the molten condition, analyses show that some of the constituents of the steel are not uniformly disseminated throughout the mass. This separation of the constituents during cooling, technically known as "segregation," is characteristic of the carbon, the phosphorus, and the sulphur. Furthermore, the segregation appears to be worst in the upper third of the ingot, so much so that many specifications now require the upper third of the ingot to be removed, and not used at all in making the articles the specifications call for. This much being stated, it is clear why our axles broke. They were made from badly segregated steel, perhaps from the rejected upper thirds of a lot of ingots, the balance of which were used for other purposes. Subsequent correspondence with the parties furnishing the axles gave good grounds for belief that such was the case. For the comfort of those who ride on railroads, it may be added that the 300 axles were at once withdrawn from service, and that since that time, a chemical and physical specification for both passenger and freight axles has been prepared, which is believed to preclude the possibility of such axles as are described above being received by the Pennsylvania Railroad.

These illustrations of the power of an analysis to explain dif-

difficulties could be prolonged to almost any extent, but I spare you. Furthermore, I should not like to be understood as claiming that every puzzle, every difficulty, or every state of affairs in nature, where the reasons for the phenomena which we find are not apparent at sight, can be explained by a chemical analysis. Our knowledge is far too limited for this. Moreover, many cases could be cited in which an analysis throws no light whatever on the situation, but notwithstanding this, an experience of some twenty years in seeking out the causes of things, as a necessary preliminary to the intelligent modification of practices and methods, in connection with a great corporation, has continually impressed me more and more, with the very great help which a properly conceived and executed analysis can give in cases of difficulty.

But again I take pride in the field of analytical work, because of the opportunity which thoughtful analytical work affords for finding new things. The careful, thoughtful, observant analyst, is constantly on the verge of either being able to add to his own knowledge, or of being able to contribute something to the general progress of our science. And here again I must be pardoned for using, as illustrations, cases which have arisen in the laboratory of the Pennsylvania Railroad Company.

A few years ago, in our laboratory, we began to get ready to make our analyses of the samples of steel which were designed ultimately to be the international standards for the analysis of iron and steel. Before starting in on these samples, however, it was deemed prudent to do a little preliminary work on some other samples with the idea in mind of seeing whether apparatus and method were satisfactory. Accordingly four separate and distinct determinations on the same sample were made for carbon, using the double chloride of copper and ammonium to release the carbon, and burning in oxygen gas. The four determinations agreed with each other within 0.01 or 0.02 of a per cent., and were regarded as fairly satisfactory. But as the work was important, and as some parts of the apparatus had not worked quite satisfactorily, it was decided to repeat the four determinations. Meanwhile a new stock bottle of solution of the double chloride had been made exactly in the manner that had been our custom for some time previous. When the second four

determinations were obtained, they differed from the first, by more than a tenth of a per cent. I need not weary you with the details of our hunt for the cause of this discrepancy, how every point in the apparatus was tested up one after another, how various modifications were tried, how combustions were made on crystallized sugar to check ourselves, and how finally we located the difficulty in the double chloride of copper and ammonium solution. These details have all been published.<sup>1</sup> Suffice it to say that as the result of this work, together with subsequent work by other chemists, it is, we believe, now generally accepted that the commercial ammonium double salt contains carbon in some form, probably pyridine, that its use as a solvent to release the carbon from iron and steel is unreliable, and that the substitution of the potassium for the ammonium double salt, overcomes these difficulties. The point which I especially want to emphasize is that in trying to do a little careful analytical work, we struck a new and apparently hitherto unsuspected source of error in one of the oldest and best established methods of iron and steel analysis.

Another illustration will perhaps make this point still more clear. In the regular course of work at one time, a silicon determination was made in a piece of tire steel, which had been sent by an officer of another railroad, for information. The figures found by our analysis were 0.14 per cent., these figures being sent to the officer above referred to. A little later word was received that an analysis of a sample from the same tire made by another chemist gave 0.28 per cent. as the content of silicon. This, of course, led us to look over our work, with the idea of finding where the cause of the discrepancy lay. A careful examination of our weights and figures showed that it was not an error of calculation. Accordingly we decided to duplicate our work, need I say, with the expectation of finding that the other chemist had made a mistake? Judge of our surprise when we found that our second analysis confirmed his figures exactly. Our first and second analyses had been made by the same method, and by the same operator, working on borings from the same bottle, and the cause of the discrepancy between the two, was not therefore, at first sight apparent. On

<sup>1</sup> *Trans. A. I. M. E.*, 19, 614.

carefully questioning the operator however, as to exactly what he did at each step of the method, a clew was obtained, which when followed out, cleared up the whole difficulty, and ultimately led to a modification of the method. The silicon in these samples was determined by what is known as Drown's method, consisting in dissolving the steel in nitric acid, adding sulphuric, heating until white fumes of the latter acid appear, to render the silica insoluble, dilution with water, filtration, washing and weighing. The difference between our two analyses consisted simply in this, that in the first case, after the dilution with water, there being considerable work in hand, the vessel was allowed to stand over night before filtration, while in the second case filtration immediately followed dilution. Subsequent work on this point showed that in this method silica is not completely dehydrated by heating in concentrated sulphuric acid, in presence of iron salts, but is apparently rendered colloidal and sufficiently dehydrated so that if filtration follows soon after dilution, fairly accurate results will be obtained. On standing after dilution, however, this colloidal, undehydrated silica, apparently goes into solution again. Indeed we were able to get on this same sample, anywhere from one-eighth up to the full amount of silicon present, by varying the time of standing after dilution, the longest time covered by our experiments being about four days.

Perhaps I may venture to give you still one more illustration of how in the course of analytical work, new and apparently hitherto unnoticed reactions may be hit upon, and modifications of methods result. Every chemist who has done much work in determining phosphorus in iron or steel, by the reduction of the molybdic acid of the yellow ammonium phosphomolybdate, and subsequent titration of the reduced solution, cannot fail to have been annoyed by the occasional failure of duplicates to agree. Apparently in the two analyses everything has been done exactly alike, and yet the results do not agree. Every thoughtful chemist cannot fail to have felt at such times, that somewhere in the method there were conditions affecting the result, that were not fully controlled. During the last six or eight months in our laboratory we have apparently struck one of these hitherto uncontrolled conditions, whose influence is not large,



and yet enough to at times, cause annoying discrepancies in duplicates, or between different chemists working on the same sample.

In order to make clear what follows, it should be stated that in the ordinary working of this method, the yellow precipitate, after careful washing, is dissolved in ammonia, and this solution then treated with sulphuric acid largely in excess, and diluted to a definite volume, in which condition it is passed through the reductor, and subsequently titrated with standard potassium permanganate. The reductor in common use consists, as is well known, of a tube of heavy glass, about five-eighths of an inch internal diameter, and about a foot long, filled with powdered zinc, the top being fitted with a funnel, and the bottom with a stop-cock. Below the stop-cock, a smaller tube carries the rubber cork, by means of which the reductor is fitted to the flask which receives the reduced solution. This smaller tube usually projects into the flask an inch or two, and it is customary to use the pump to draw the liquid through the reductor. This much being premised, we may say that in a communication from Mr. Porter W. Shimer, one of the members of the Sub-Committee on Methods of the Committee on International Standards for the Analysis of Iron and Steel, he, among other things, called attention to the fact that when making a number of determinations on the same sample, all other things being the same, he got a reduced solution that required more permanganate if he prolonged the small tube below the stop-cock in the reductor, nearly to the bottom of the flask, than if this small tube projected only an inch or two into the flask. This statement brought afresh to our minds, a thought that every one who has worked much with molybdic acid must have had; *viz.*, that reduced molybdic acid is very easily reoxidized. We accordingly determined to find out, if possible, whether this was actually the case and, if so, how much this difficulty might amount to. Accordingly, a stock solution of ammonium molybdate dissolved in water, was prepared, and a number of aliquot parts of this solution measured out. Now, obviously, there are two chances for the reduced solution to become oxidized by exposure to the air. One of these is from the air in the flask during the reduction, and on the other from the outside air during the



titration. Without going into minute detail, it is perhaps sufficient to say that when we reduced an aliquot part of our stock solution, using the short tube of the reductor, and adding the permanganate drop by drop, with continual agitation during the whole titration, we used 22.7 cc. of our standard permanganate, all figures given being a mean of a number of closely agreeing determinations. When now we made the reduction the same as before, *viz.*, with the short tube of the reductor, but titrated by allowing about ninety-five per cent. of the permanganate required to run into the flask before agitation at all, and finishing the titration drop by drop, we used 23.1 cc. of permanganate; in other words, so sensitive is a reduced solution of molybdic acid, that it is easy by varying the mode of titration to introduce considerable error. Prolonging now the tube at the bottom of the reductor as suggested by Shimer, which would result, as is apparent, in a diminished exposure of the reduced solution to the air in the flask before titration, we found our aliquot part to use up 23.6 cc. of permanganate. But even with the prolonged tube, there is some exposure of the reduced solution to the air during the reduction. Accordingly, on the suggestion of my principal assistant, Mr. F. N. Pease, we put a measured amount of standard permanganate solution into the flask which was to receive the reduced solution, more than sufficient to react with it, and then prolonged the tube from the reductor, to dip below the surface of this permanganate. Obviously with this arrangement the reduced solution is entirely prevented from air exposure. On making the reduction and titrating the excess of permanganate with standard solution of ferrous sulphate, it was found that the aliquot part had now used up 24.1 cc. of permanganate, an extreme difference in amount of permanganate used under the varying conditions described, of nearly six per cent. Obviously, if two chemists were working on the same sample of molybdic acid, one employing the manipulation first described, and the other that last described, the discrepancy between them would be serious. The discrepancy on phosphorus in steel, while the same in percentage, is very much smaller in actual figures, but still enough to be annoying. The work above referred to is not yet quite finished, but enough has already been done to demonstrate that the ordinary method of determining

phosphorus in steel can be advantageously modified in the interests of greater accuracy; and also, although not yet rigorously demonstrated, there are strong indications that molybdic acid ( $\text{MoO}_3$ ), is always reduced by zinc to  $\text{Mo}_2\text{O}_3$ , and that the more complex formulas,  $\text{Mo}_3\text{O}_8$ ,  $\text{Mo}_4\text{O}_{11}$ , etc., so commonly given as representing this reduction, simply mean that the conditions under which these formulæ were obtained, permitted the reoxidation of the reduced solution to the extent indicated.

There is another phase of this question we are discussing, "The Dignity of Analytical Work," which will perhaps bear a few words. It seems to be universally conceded that the brain that plans and guides is worthy of more honor than the hand that executes; the general deserves more than the private soldier; the architect, than the builder; the investigator who plans the work, than the chemist who makes the analyses. Few will object to such a distribution of rewards as this, and certainly no one will claim that a chemist who, machine-like, simply follows directions, without thought or interest in the matter, can fairly claim recognition for anything more, perhaps, than manipulative skill and honesty. But, on the other hand, is it fair to say that such analysts can truly be called analytical chemists? Does not the genuine analytical chemist embody within himself, not only the capacity of brain to wisely plan his method of attack, to conceive which one of the possible reactions in the case it will be best to employ, but also the requisite manipulative skill, to carry out the line of action decided upon? To my mind, these two things, *viz.*, the brain power necessary to plan the work, together with the continual activity of the brain while the work is going on, and the skilled and trained hand requisite to do the work, are necessarily coexistent at the same time in the good analytical chemist, and woe be that chemist who tries to put them asunder. The analyst whom chance or the exigencies of earning his livelihood have thrown into a situation, where day after day he must, for a time at least, do the same thing over and over again, and who does not, even in this situation, use his brain constantly, does not each time he adds a reagent think what is going on in the beaker, does not each time he washes a precipitate think what he is washing out, does not every time he makes a weight take a genuine interest in the result, and even the

hundredth time that he makes the same determination, is not on the lookout for some flaw in the method he is using, or some possible new reaction in connection with it, such an analyst I say, will stand a good chance to remain a routine chemist all his life.

On the other hand, what shall we say of those chemists who plan out a line of investigation, and are content not to make the necessary analyses themselves? We are quite well aware that at the present time this is a very common method of making investigations, and we can, of course, understand that pressure of other duties may make it impossible to pursue investigations in any other way. But we cannot regard this state of affairs as, to say the least, anything less than unfortunate. If we may trust our own experience, the time spent in making the analyses required by one line of attack on a stubborn problem is most valuable, in the opportunity which it affords for carrying the problem in mind, and planning out other lines, in case the one in hand does not succeed. Moreover, still more valuable is it to make the analyses yourself, in that while doing so, you so frequently get suggestions from the work that are the very ones upon which final success depends. I wish there was time to illustrate this point as its importance deserves, but the history of chemistry and your own experience will have to furnish them to you. To our minds it is hard to overestimate the importance, especially to a young investigator, of his doing his own analytical work for himself. If we read rightly, this was the almost universal habit of the old masters of our science, and we greatly fear that those chemists, who from choice delegate their analytical work, will find after years of such delegation, that their reward of successful investigations is very small.

A single thought farther. At the present time so much applied chemistry is either based on analytical work, or has analytical work as an almost essential constituent of its existence, that in a paper discussing analytical work, a few words may not be amiss, on the relations between pure and applied chemistry. Without wishing to touch in the slightest degree on mooted or disputed questions, it may not be unfair to say, that while the applied chemist does truly, as the name indicates, in the mass of his work, utilize or apply the discoveries of others,

to useful effect, it does not at all follow, that in the field of applied chemistry, no discoveries yet remain to be made. It is certainly not too much to say that no thoughtful chemist has ever worked for any length of time in any field of applied chemistry, without finding himself surrounded with problems involving new and unknown reactions, with problems, am I not safe in saying, requiring for their solution, as good appliances, as deep study, and as keen thought, as any that occupy the minds of the pure chemists. These problems continually force themselves upon him, and his only regret in the matter is, that the time at his disposal does not permit him to solve them as fast as they arise. A prominent feature of these applied chemistry problems, remains to be mentioned; *viz.*, they generally have immediate useful applications, as soon as they are solved. The applied chemist usually makes an excursion into the unknown, because some difficulty has arisen in the course of his regular work, or because some new, more rapid, or more economical method of accomplishing results, is desired. He may succeed in finding a new reaction, or in utilizing an old one, as the basis of a successful commercial process, or in modifying a manufacturing method in the interests of both economy and speed. But whatever his work, the immediate useful application of the information he secures, is both his stimulus and guide. He may not be able from lack of time to follow his work up, and find the complete relations of the facts ascertained to the other branches of chemistry, but this is his misfortune rather than his fault, and this condition of affairs, *viz.*, being unable to follow out to completion, lines of research one started on, is, if we understand the matter rightly, not characteristic of the applied chemist alone. This much being said, let us ask in what respects the pure chemists resemble or differ from those who work in the field of applied chemistry. They certainly are alike in this, that neither of them can devote his whole time to original work. Both must devote no small portion of their energy to other lines than making investigations. There may have been a time in the history of chemistry when investigators were so fortunately situated, that they could devote their whole time and energy to finding out new truth, and giving their results to the world. All honor to such investigators. Moreover, we all know that

occasionally an appropriation of funds or an endowment is made for research in some special field. But truly would it not be too much to say, that the work of any large percentage of the pure chemists of to-day, is the result of such fortunate circumstances? Furthermore the pure and applied chemists are alike in that in their original work, both are seeking for the truth, and if they are successful, both are adding to the sum of human knowledge. They differ, as it seems to me, principally in this: First, the researches of the applied chemists being largely made in the interests of corporations or manufacturing establishments, the results of these investigations, in many cases, are not at once available to the world, except in so far as they lead to diminished cost of production. Those who have paid for these researches, naturally feel that they should be allowed a period of time at least, to recoup themselves for their expenditures and so they protect themselves either by patents or secrecy. But this is only a knowledge of the truth deferred. Sooner or later the results of the investigations of all applied chemists, are added to the great body of accumulated chemical knowledge. The pure chemist, on the other hand, at once gives the results of his investigations to the world, and is quite content if the publication of his researches shall bring him as his reward, a modicum of appreciation from his fellows. Second, in their original work, the pure chemists differ from the applied chemists in the ulterior purpose for which the investigation is undertaken. As has already been stated, the applied chemist usually undertakes an investigation, tries to find new truth with the avowed purpose of at once utilizing this truth as soon as it is found. Not so the pure chemists. The problems which they attack and solve so successfully, have no necessary relation to subsequent utility. The truth which they discover, and put on record, may be found to be useful at some time, but its possible immediate utility or non-utility is not taken into consideration by the pure chemist, either in his choice of a subject for investigation, or in the prosecution of his work. The truth for the truth's own sake, is his motto and guiding star.

If we have diagnosed the case correctly, then the principal differences between the pure and applied chemist are, that the latter withholds the results of his work from

the world for a period of time, while the former gives his at once, and that the latter is, in his original work, seeking for truth that is at once useful as soon as it is worked out, while the former neither knows nor cares whether the truth that he discovers, is either now or at any future time turned to practical or useful effect. Let me not be misunderstood. I am not attempting to belittle in any sense the work of the pure chemists. They are worthy of all honor and respect. But on the other hand, I am not at all willing to have the work of the applied chemists made light of or treated as though it were in an inferior field. To my mind there is no occasion for either to belittle the work of the other. The field of chemistry is so broad, the amount of unoccupied ground in every branch of the science is so great, that there is neither time nor energy for struggling as to who is greatest or who is least, but in whatever line a man's tastes, opportunities, or the force of circumstances may lead him, whether as a pure or an applied chemist, whether organic or inorganic, whether theoretical, physical, or agricultural, whether analytical or synthetic, provided in his mind at all times, the love of the truth is above all, and honest work is being done, he is worthy of recognition, honor, and respect.

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## ALKYL BISMUTH IODIDES AND BISMUTH IODIDES OF VEGETABLE BASES.<sup>1</sup>

BY ALBERT B. PRESCOTT.

Received November 20, 1897.

THE common alkyl ammonium iodides, with solutions of the bismuth salts, give bright-colored precipitates. As formed by quaternary methyl or ethyl ammonium iodides, the color is orange-yellow in most cases, usually lighter when obtained with bismuth chloride, and darker when obtained with bismuth nitrate. When fully formed by excess of the organic iodide, in bismuth solution not strongly acid, the precipitation is amorphous and so nearly complete that when the filtrate from a test-tube portion is evaporated to dryness and the residue ignited and treated with solvent acid, hydrogen sulphide fails to

<sup>1</sup> Read before the American Pharmaceutical Association, in the report of a special committee, at Minnetonka Lake, August, 1897, and to be published in the Association Proceedings for this year.

blacken the liquid. Strong mineral acids slowly decompose these colored precipitates, liberating iodine.

What has been known as Dragendorff's reagent for alkaloids is a potassium bismuth iodide, prepared by dissolving precipitated bismuth iodide in a concentrated solution of potassium iodide acidulated with hydrochloric acid, and known as giving reddish-colored precipitates in solution of the salts of the alkaloids. On trial with pyridine salts, a corresponding precipitate was obtained, dark orange-red and voluminous. Kraut<sup>1</sup> has reported the piperidine compound, to which all these are analogous.

These organic bismuth iodides are not perfectly proof against decomposition by much water; they are sparingly soluble in ethyl or amyl alcohol, insoluble in glacial acetic acid, in ethyl ether, in chloroform, and in benzene.

The tetramethyl ammonium bismuth iodide crystallizes from hydrochloric acid, that of sp. gr. 1.19 diluted with an equal measure of water. Also from potassium iodide solution acidulated with hydrochloric acid. The pyridine and the alkaloid bismuth iodides crystallize from alcohol. In all these cases the crystals are clearly hexagonal and easily obtained.

Both the amorphous and crystalline forms are stable in the air. A sample of tetramethyl ammonium bismuth iodide remained constant in weight at 130°; atropine bismuth iodide melts, but, at 98° C. holds constant weight.

Reducing agents, as potassium thiosulphate, do not alter these bismuth iodides. Tetramethyl ammonium bismuth iodide, precipitated from ten per cent. solutions both of the organic iodide and bismuth iodide, washed with hydrochloric acidulated water, then with pure water till washings gave no residue, then with alcohol, and lastly with ether, and dried at 110°, gave figures as follows :

Analyses I and II were of the same preparation, III and IV from other preparations made at different times.

	I.	II.	III.	IV.	$N_2(CH_3)_{11}HBi_2I_7$ .
Iodine . . . . .	58.71	58.29	60.79	....	59.22
Bismuth . . . . .	27.08	....	....	....	27.07
Carbon . . . . .	8.69	8.68	8.58	8.06	8.82
Hydrogen . . . . .	2.16	2.12	2.30	2.37	2.08
Nitrogen . . . . .	2.81	2.73	....	....	2.81

<sup>1</sup> *Ann. Chem.* (Liebig), 210, 310-327.



The pyridine bismuth iodide, prepared from a pyridine salt by Dragendorff's reagent and crystallized from alcohol, on elementary analysis gave figures as follows :

Different preparations.	I.	II.	III.	$(C_5H_5N)_2(HI)_2BiI_6$ .
Iodine .....	63.98	62.84	62.24	63.59
Bismuth .....	23.36	23.72	....	23.18

Kraut<sup>1</sup> found analogous composition for piperidine bismuth iodide.

The corresponding atropine bismuth iodide gave results as follows :

Several preparations.	I.	II.	III.	$(C_{17}H_{23}NO_2)_2(HI)_2BiI_6$ .
Iodine .....	46.99	47.03	46.51	46.96
Bismuth .....	18.82	18.67	18.53	17.22
Carbon.....	23.22	23.62	23.69	25.23
Hydrogen.....	2.87	3.02	2.94	2.96
Oxygen .....	8.10	7.66	8.33	7.63

The carbon is too low for the theory, so that the figures approach to those of  $(C_{17}H_{23}NO_2)(HI)BiI_6$ .

The brucine compound gave, for  $(C_{22}H_{27}N_3O_4)_2(HI)_2BiI_6$ , of iodine 41.10 and 40.88 per cent. against 41.56 by calculation from the formula.

The corresponding strychnine salt gave, for iodine, 44.02 and 44.65 per. cent. against 44.48 by calculation from the formula.

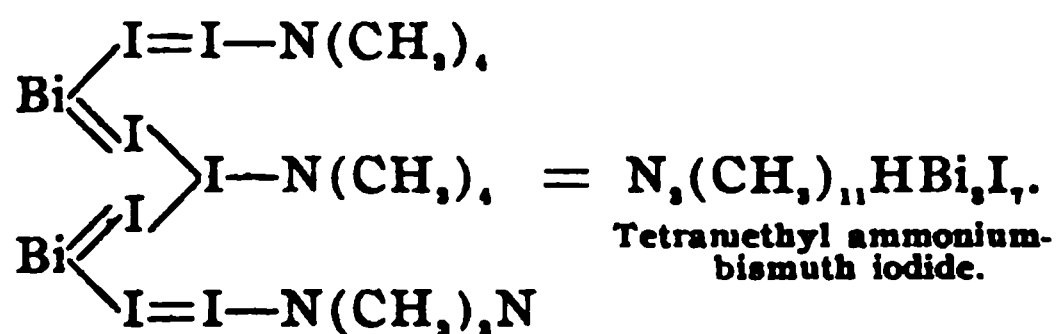
In the results of the work I have done upon the perhalides and double halides of nitrogen bases in the last two or three years, everything goes to support the theory that two or more halogen atoms link to each other with an (uneven) valence of more than one, so as to connect one group of atoms with another. Iodine, especially among the halogens, serves as a binding element in the coupling of other elements with each other, as well as in massing its own atoms together in a heavy periodide, as a swarm of bees hang upon the bough of a tree. In the double iodide structure, where iodine links one base to another base, serving between positive and positive, with iodine not in excess of the "normal" number of its atoms, potassium thiosulphate will not take iodine out of the compound. In the periodide structure where iodine links a base to additive iodine, serving between a positive and a negative group, potassium thiosulphate promptly

<sup>1</sup> *Ann. Chem.* (Liebig), 210, 310-327.



removes all the additive iodine, leaving a normal single iodide. These generalizations apply to the dipyridine alkyl iodides reported with determinations of molecular weight by Mr. Flintermann and myself in 1895.<sup>1</sup> Also to the various monopyridine alkyl normal iodides<sup>2</sup> and to the numerous periodides.<sup>3</sup> In the compounds of additive iodine, as in double iodides, the results of analysis are in most cases consistent with an uneven valence of iodine, indeed with its trivalence. But there are a very few periodides well determined by Mr. Trowbridge as monopyridine compounds, in which, in our present knowledge, an even numerical valence of iodine is indicated.

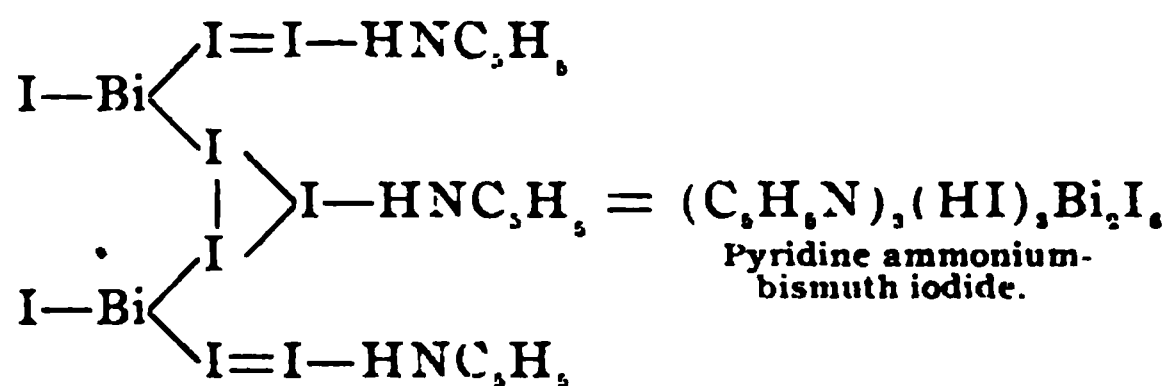
The bismuth iodides of nitrogen bases reported in this paper, both those of fatty alkyls on the one hand and those on the other hand of pyridine and pyridine-derived alkaloids, all evidently conform in their analytical content to the regular iodine-linking structure, the structure common both to double iodides and periodides, as shown in the following proposed constitutional formula. In the case of the quaternary ammonium bismuth compounds, with the prevailing bismuth characteristic of losing halogen in presence of water, the wash-water being found tinged with iodine, each bismuth atom is directly bound to only two atoms of iodine, while in the pyridine-formed compounds the bismuth atom is bound to three atoms of iodine in each instance, bismuth and iodine valencies being always the same. Again, the fatty ammonium compounds, less stable as they are, show a variation from the quaternary to the tertiary base type, in one of the three nitrogen basal groups of the molecule. This doubtless comes about by reaction of water to form methyl alcohol as a by-product, leaving hydrogen in place of methyl in the main product.



<sup>1</sup> This Journal, 18, 28.

<sup>2</sup> Prescott and Baer, 1896: *Ibid.*, 18, 247.

<sup>3</sup> Prescott and Trowbridge, 1895: *Ibid.*, 17, 859; P. H. Trowbridge, 1897: *Ibid.*, 19, 322; Trowbridge and Diehl, 1897: *Ibid.*, 19, 558.



Analogous to  
 $(\text{C}_{17}\text{H}_{23}\text{NO}_3)_3(\text{HI})_3\text{Bi}_2\text{I}_6$ .  
 Atropine bismuth iodide.

The alkaloidal bismuth iodides are not quantitatively uniform enough to be entirely satisfactory for alkaloidal assay, but are more stable and uniform than the alkaloid mercuric iodides formed by Mayer's reagent. On the other hand, they are more bulky, less easy to gather in a compact mass, less manageable in filtration. On the whole, so far as found, Dragendorff's reagent gives no general advantage over that of Mayer, though I am well aware how unsatisfactory the latter has been found in the hands of analysts.

For the execution of the work upon tetramethyl ammonium bismuth iodide, I am wholly indebted to Mr. H. E. Brown; for that upon the bismuth iodides of pyridine and the alkaloids to Mr. O. C. Diehl. A further study of the reactions of the halides of bismuth upon representative organic bases is now left to Mr. Brown.

ANN ARBOR, MICH., AUGUST, 1897.

## THE ACTION OF SULPHURIC ACID ON MERCURY.

BY J. R. PITMAN.

Received November 18, 1897.

THE following statement is made by Messrs. Baskerville and Miller, in a previous number of this Journal (19, 874): "A qualitative experiment showed that mercury decomposed concentrated sulphuric acid at the ordinary atmospheric temperature, about 20° C."

As a large amount of my work consists in the use of nitrometers, this statement was of considerable interest to me; however, believing their conclusions to be erroneous, the following simple tests were tried: Apparatus used, a Lunge nitrometer, with separate reading burette; the temperature at all times was

about 22° C.; the amount of mercury was from eight to ten times that of the acid (by volume).

First experiment: Thirty cc. of concentrated sulphuric acid was run into the generating bulb, and allowed to stand for forty-eight hours, being shaken at intervals; I was unable to get any gas at all under these circumstances, and there was apparently no reaction between the mercury and the sulphuric acid. Thinking that possibly the presence of air might have some effect upon the reaction, I next measured a certain quantity (about fifty cc.) of rather damp mercury; this was run into the generating bulb and thirty cc. of sulphuric acid as well; after shaking at intervals for twenty-four hours, the air was remeasured and found to have *lost* four-tenths cc.; this loss was probably due to the presence of considerable moisture in the air when first measured; as a check this same air was conducted (thoroughly dried from its contact with the sulphuric acid) from the reading burette into another generating bulb, drawing in thirty cc. of concentrated sulphuric acid, and shaking again, as before, for about twenty-four hours, with a result of a loss of less than 0.05 cc., which is an error that might occur in any test.

In order to try the effect of the preponderance of sulphuric acid, one part of mercury to seventy by volume of concentrated sulphuric acid was taken (sp. gr. 1.84), introduced into a flask, and shaken violently for some time; no mercuric sulphate was formed, nor was there appearance of any other reaction; this was at a temperature of 25.5° C. From these experiments it is apparent that there is no reaction between mercury and sulphuric acid at ordinary temperature, and if Messrs. Baskerville and Miller found a reaction as they state, it must have been by means of some different method.

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## ON THE DETERMINATION OF FAT AND CASEIN IN FECES.

BY E. E. SMITH.

Received November 15, 1897.

IN the November number (1897) of this Journal, Herman Poole writes, in regard to this subject, that in searching the literature he "found nothing at all which would give even a fairly

approximate idea of the percentage of fat and casein." I desire to call this writer's attention to the following :

In studying the stools of jaundiced patients, Müller<sup>1</sup> determined the fats by the following method : The dried and finely powdered material is extracted with ether for three days, the residue from the extract washed with successive portions of warm water, dried and weighed, and divided into portions which are used (1) for the determination of ash by ignition ; (2) for the determination of free fatty acids by titration in alcohol-ether solution with standard alcoholic potassium hydroxide, phenolphthalein indicator ; (3) for the determination of the melting- and congealing-points ; and to these may be added, if desired, (4) for the determination of the unsaponifiable residue.

The residue of the original material is digested with hot alcoholic hydrochloric acid, dried and again extracted with ether, and the residue from the extract either titrated or weighed, giving the fatty acids present in combination with alkaline earths. From these data are calculated the neutral fats, the free fatty acids and the soaps.

A serious objection to the method of extracting the dried and powdered material probably exists, for it has recently been demonstrated<sup>2</sup> that some substances, notably meat and milk products, give up only a small portion of their fat to the ether when extracted in this condition. Doubtless, then, more accurate results are obtained by Hoppe-Seyler's method of adding water to the fresh material to bring it to the consistence of a thin mush, evaporating somewhat to remove volatile substances and using the material in this condition for the extraction of the fats.

It may also be admissible for me to call attention to the long-standing discovery of Flint,<sup>3</sup> which the writer has apparently overlooked, that normally there is no cholesterol in feces. It is present in the bile, but in the upper intestinal tract is converted into a chemically different, though allied substance called, by Flint, stercorine. Flint's discovery has recently received confirmation in the observations of two European investigators,<sup>4</sup> who have redescribed stercorine under another name. There appears to be no doubt of the identity of their product and Flint's<sup>5</sup> stercorine.

<sup>1</sup> F. Müller : *Ztschr. klinische Med.*, 1887, p. 43.

<sup>2</sup> Dormeyer : *Pflüger's Archiv. f. Physiol.*, 61, 341.

<sup>3</sup> Flint : *Physiology of Man*.

<sup>4</sup> Boudzynski and Humnicki : *Ztschr. physiol. Chem.*, 22, 396.

<sup>5</sup> Flint : *Ztschr. physiol. Chem.*, 23, 363.

# THE RELATIVE SENSIBILITY OF PLANTS TO ACIDITY IN SOILS.

BY WALTER MAXWELL.

Received November 23, 1897.

**T**HE degree of acidity in soils is relative, and is largely controlled by climatic conditions. In temperate zones, due to the more moderate means in temperature and rainfall, this matter of acidity does not necessarily engage as much attention in agricultural considerations. In subtropical and tropical conditions, in which the writer is engaged, and where the mean annual temperature is over  $21^{\circ}$  C., and the yearly rainfall varies between twenty inches on the leeward side of the islands, and 200 inches (17.5 feet) on the windward uplands, the matter of soil acidity demands primary and careful consideration.

Our observations were made not only in order to obtain precise knowledge concerning the relative sensibility of various plants, and families of plants, to acid conditions, but also to indicate that the errors and confusion at present existing, concerning the forms in which plants assimilate nitrogen, may be in part due to this behavior of plants in relation to acidity.

In another publication<sup>1</sup> we selected, among others, as an example, a tropical wood fern, which was growing in conditions of extreme soil acidity, such as the sugar-cane could not exist in. We used the analysis of this fern, the green leaves of which contained four-tenths per cent. nitrogen, to show that "one of the two theories must be wrong, and that the nitrifying organisms in soils can carry on the nitrification of organic nitrogen in acid media, or that the fern must take up nitrogen in a non-nitrified form."

The conditions of the situation have obliged us to make examinations, the results of which show that certain common agricultural varieties of plants live and thrive in soils where others totally fail; and that the success or failure of the respective varieties can be due to the inability of given plants to withstand a degree of soil acidity in which other plants reach a considerable and even normal growth; and may be quite independent of the mode and elements of plant nutrition.

The experiments which furnished the given data were

<sup>1</sup> Reports of the Hawaiian Experiment Station, 1896.

arranged and conducted as follows : Two tubs having a diameter of twenty-four inches, and a depth of twenty inches, and perforated bottoms, which were covered with linen cloth, were each filled with 120 pounds of air-dried soil of moderate fertility, having a neutral behavior towards acid and alkaline tests. These tubs were placed in tin pans which were six inches deep, the perforated bottoms of the tubs being raised four inches above the bottoms of the tin pans. The tin pans were filled with water up to the level of the perforated bottoms, and the water was kept up to that level until the soil in the tubs had absorbed moisture to saturation, the water absorbed being 48.2 per cent. on the water-free weight of the soil. To tub No. 1 enough citric acid was added to make the whole volume of water absorbed a one-tenth per cent. solution. To tub No. 2 citric acid was added to make the absorbed water a one-fiftieth per cent. solution. In each of the tubs seventeen varieties of seeds were planted, these being planted in a circle, and equal distances apart. The seeds germinated quickly, were up within four days, and had a healthy appearance. After the plants were up, and one inch high, the mode of applying the acid was changed. When the acid was applied in the water absorbed by capillarity from the tin pans, it was not equally distributed through the mass of the soil, but was more or less fixed by the bases in the soil at the bottom of the tubs, and did not reach the plants. Therefore the acid was dissolved in water and applied around the plants at the surface. This was controlled by determining the loss of water from the tubs by evaporation, and replacing the lost water, with the weight of citric acid dissolved in it necessary to bring up the whole volume of water in the tubs to one-tenth per cent. and one-fiftieth per cent. solutions respectively. This was repeated every fourth day, the acid solution being applied by our field assistant, E. G. Clarke, with a pipette, and in strictly equal quantities to each plant. With this detailed description of the mode of applying the citric acid to the tubs, the results may be given, which are found in the following tables :

## A. CRUCIFERA.

*(Tub No. 1. Strength of Acid one-tenth per cent.)*

Name of plant.	Planted.	Up.	Failed.	Development.
Black mustard.....	May 27	May 29	June 15	Three inches high
White mustard ....	"	" 29	" 15	"
Beet.....	"	" 31	" 11	"
Mangel wurzel.....	"	" 31	" 11	"
Rape .....	"	" 30	" 17	"
Carrot.....	"	June 3	" 17	Four "

*(Tub No. 2. Strength of Acid one-fiftieth per cent.)*

Name of plant.	Planted.	Up.	Failed.	Development.
Black mustard.....	May 27	May 29	June 15	Three inches high
White mustard ....	"	" 29	" 11	"
Beet .....	"	" 31	" 11	"
Mangel wurzel.....	"	" 31	" 11	"
Rape .....	"	" 30	" 11	"
Carrot.....	"	June 3	" 17	Five "

## B. LEGUMINOSAE.

*(Tub No. 1. Strength of Acid one-tenth per cent.)*

Name of plants.	Planted.	Up.	Failed.	Development.
White lupine...	May 27	May 30	July 16	1 foot high
Cow bean.....	"	" 30	Aug. 31	7 feet 2 inches long (No seed)
Windsor bean ..	"	June 3	Aug. 12	3 feet long
Winter vetch...	"	May 31	July 9	2 feet long
Crimson clover.	"	" 30	June 17	3 inches high
Alfalfa.....	"	" 29	" 15	3 inches high

*(Tub No. 2. Strength of Acid one-fiftieth per cent.)*

Name of plants.	Planted.	Up.	Failed.	Development.
White lupine...	May 27	May 30	July 21	1 foot 2 inches long
Cow bean .....	"	" 30	Aug. 30	6 feet long (No seed)
Windsor bean ..	"	June 3	" 12	3 feet long
Winter vetch...	"	May 31	" 4	3 feet long
Crimson clover.	"	" 30	June 17	3 inches high
Alfalfa.....	"	" 29	" 11	3 inches high

## C. GRAMINAE.

*(Tub No. 1. Strength of Acid one-tenth per cent.)*

Name of plants.	Planted.	Up.	Result.	Development.
Pearl millet....	May 27	May 30	Matured	4 feet 1 inch long and formed seed
Wheat.....	"	"	Failed	1 foot 3 inches high
Maize .....	"	"		3 feet 6 inches high Formed flowers but no seed
Oats.....	"	"	Failed	8 inches high
Barley .....	"	"	Failed	8 inches high

*(Tub No. 2. Strength of Acid one-fiftieth per cent.)*

Name of plant.	Planted.	Up.	Result.	Development.
Pearl millet.....	May 27	May 30	Matured	5 feet 4 inches high and formed seed
Wheat.....	"	"	Failed	1 foot 2 inches high
Maize .....	"	"		Formed flowers but no seed
Oats.....	"	"	Failed	6 inches high
Barley.....	"	"	Failed	11 inches high

The crucifers succumbed almost immediately to the action of the acid, the one-fiftieth solution acting almost as effectually as the one-tenth solution. This behavior of the crucifers under artificial treatment with citric acid corresponds to certain general observations upon the growing of root crops in non-aerated and sour lands.

The lupine, bean, and vetch struggled hard and long against the acid action, but none of these fully matured, or formed seed. The crimson clover and alfalfa succumbed as rapidly as the crucifers, showing that the clovers cannot bear an acid soil, and explaining one cause of the extreme "hunger" of the clovers for lime.

The gramineae showed a very variable behavior in relation to the acid. The wheat, barley, and oats failed almost completely, although none of these actually died. The maize grew well, had a strong and deep green-colored blade, and reached a moderate size, forming a full blossom, but no seed. The pearl millet distinguished itself from all the other varieties. Its growth was steady and quite normal, as compared with a plat of millet growing in the field near by, which it actually exceeded in development, reaching five feet five inches in height. Five large heads matured, which contained a finer grade of seed than was originally planted. A special test was made with the millet, in which the plant was treated every fourth day with a one per cent. solution of citric acid. This strength of solution kept the young plant, which was three inches high, at a standstill for three weeks. After that time the plant appeared to accommodate itself to the intense acidity, began a further growth, and was two feet high when the experiment was stopped. (A photograph was taken of this example.)

Considering the relation of these observations to common findings in the field, it may be said that maize is being planted with



some success in our upland, acid soils, and millet will now be tried. The effects of acidity upon the crucifers and certain legumes, have been noted in soils notably less sour than most of the upland soils of these islands. The Director and Agriculturalist of the Rhode Island (U. S.) Experiment Station, Professor Flagg, in a communication concerning a sample of soil sent to the laboratories of the writer, says: "We found all this soil acid when tested with litmus paper; so much so that timothy and clover, barley, beets, spinach, lettuce, and a few other plants, failed to thrive without the use of air-slaked lime to correct the acidity."

These observations, which are only a part of extensive investigations that will be published shortly, show the extreme difference in degree of sensibility of the various agricultural plants to soil acidity. They also indicate with what ease a failure in growth of one plant can be attributed to some trouble in plant nutrition, when it may be wholly due to the inability of the plant to bear the acidity of the soil, which is illustrated, as has been shown, by the power of other plants to thrive in the same medium.

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## METHODS AND SOLVENTS FOR ESTIMATING THE ELEMENTS OF PLANT FOOD PROBABLY AVAILABLE IN SOILS.

BY WALTER MAXWELL.

Received November 23, 1897.

IN framing a method, and in the selection of solvents for estimating the proportion of plant food probably available in soils, it appears necessary to be wholly guided by a precise observance of the agencies by means of which the insoluble soil-materials are being daily changed by the processes of nature in the field, into forms in which they can be used by growing plants.

The processes by which the food elements are prepared in nature are altogether chemico-physiological; and for this reason the problem cannot be primarily considered from an analytical standpoint.

The solvent agents operating in nature's processes are, in addition to water, the acids moving in the sap of living organ-

isms, and being emitted through the membranes of their roots, the chief one, so far as our present knowledge goes, being carbonic acid ; and, more important, the acids which result from the decay of vegetable matter upon and within the soil. The acids that are formed when plants, roots, and fruits decay are the simple organic acids,—carbon acids ; and the amido acids,—carbo-nitrogen acids. Consequently, the acids in living, and produced by dying, plant organisms are carbon acids, with or without nitrogen. In the complete decay of vegetable matter, however, these organic acids are resolved into ultimate mineral bodies ; the carbon into carbonic acid, and the nitrogen of the amido acids into nitric acid or nitrogen, the simple forms in which these were primarily taken from the air to build up the plant organism. Consequently, the amounts of carbon and of nitrogen contained in the composition of plant organisms are respectively the measure of the relative amounts of simple carbon acids and of amido acids that can be produced in vegetable decay ; and of the amounts of carbonic acid and nitric acid that finally result from that decay, and which act as solvent agents upon the soil. The minute amount of sulphuric acid, and the still more minute portion of phosphoric acid, that are formed from the sulphur in the nucleins, and the phosphorus in the phosphoglycerides (lecithines), are unnoticed in these considerations. Also the basic action of the amidogen group ( $\text{NH}_2$ ) contained in the amido acids, which has been indicated in our investigations, is reserved for notice until a statement of results in detail is made. In the absence of elementary determinations of carbon in the composite structure of plants, these estimations having been confined to constituent bodies some other mode has to be used for arriving at an estimation of the proportion of that element contained in plant organisms ; and, at the same time, of the relative proportion of nitrogen. This is done by ascertaining the amount of the constituents of plant organisms that are composed of carbonaceous bodies not containing nitrogen, and the proportion of these bodies that do contain nitrogen. The carbonaceous bodies free from nitrogen are the so-called nitrogen-free extract matters, the fiber, and, for the present purpose, are added the fats. The bodies containing nitrogen are collectively considered as proteids. The relative amounts of these non-

nitrogenous and nitrogenous constituents found in a broadly representative series of agricultural growths are set forth in the following table :

Kinds of growths.	No. of ex- amples.	Proteids.	Fiber.	Nitrogen-free extract matter.	Fats.
		Per cent.	Per cent.	Per cent.	Per cent.
1 Legumes and cereals.	32	8.0	27.6	51.0	3.1
2 Roots and bulbs.....	14	13.9	10.5	64.5	3.1
3 Grain and other seeds	45	12.9	2.3	79.5	4.4
Means.....	91	11.6	13.5	65.2	3.5

If the third series (the seeds) should not be included in the average, for the reason that the grain and seeds are not allowed to return directly to the soil, the means will remain nearly the same, since the large proportion of the extract matters in seeds is offset by the small amount of fiber. These data show that in the 91 examples of vegetable growths we have :

	Per cent.
Nitrogen-free carbonaceous bodies.....	92.2
Nitrogenous carbonaceous bodies .....	11.6

The nitrogen-free carbonaceous bodies, including the small amount of fats, may be considered as bodies containing six atoms or parts of carbon  $(C_6H_{10}O_6)$ . The proteids, in which the elementary analysis finds sixteen per cent. of nitrogen, with fifty-four per cent. of carbon, are bodies in which, according to the relative atomic weights, about three parts of carbon are associated with one part of nitrogen. The relation of the carbon and nitrogen present in those organisms, then, may be expressed thus :

			Parts of carbon.
Nitrogen-free carbonaceous bodies ..	82.2 per cent.	$\times 60 =$	493.2
Nitrogenous carbonaceous bodies ...	11.6	$\times 3 =$	34.8
			528.0
			Parts of nitrogen.
Nitrogenous carbonaceous bodies.....	11.6	$\times 1 =$	11.6

These data show that in the composition of the plants, roots, and seeds stated there are forty-five parts of carbon to one part of nitrogen. Therefore, in the decomposition of those organisms there must finally be produced forty-five parts of carbon dioxide and one part of nitric acid.

Nitric acid is a more immediately active solvent than carbonic acid, and will dissolve soil material rapidly while its action lasts. The duration and measure of its action, however, are fixed by the quantity, and can extend only to the point of neutralization with the bases it acts upon, which is the case with the carbonic acid. Moreover, nitric acid is a monatomic acid, whilst carbonic acid is a diatomic acid; which thus doubles the solvent power of the forty-five parts of carbon, and lowers the possible action of the one part of nitric acid to only  $\frac{1}{45}$  part of that of carbonic acid, providing both acids exercise their action on the soil bases to neutralization.

These considerations have appeared to the writer to constitute the nature of any method, and the character of any solvent whose action can approximately compare with the processes operating in the field. Their reasonable nature has been amply endorsed in a course of work in which methods were adopted, from which mineral acids were excluded, and simple carbon acids and amido acids were exclusively used as solvents. The results, which form only a part of a broad investigation which is being carried on of Hawaiian soils, and which have been obtained with the aid of the associated labors of our first assistant chemist, J. T. Crawley, and C. F. Eckart, second assistant chemist, will be published in later issues of this Journal.

LABORATORY OF THE HAWAIIAN SUGAR PLANTERS' ASSOCIATION.

## A DELICATE TEST FOR THE DETECTION OF A YELLOW AZO DYE USED FOR THE ARTIFICIAL COLORING OF FATS, ETC.<sup>1</sup>

BY JOSEPH F. GEISLER.

Received January 5, 1898.

THE food laws of several of the states prohibit the use of coloring-matter in oleomargarine, and inasmuch as the presence of artificial coloring-matter in many cases constitutes the only infraction of these particular laws, simple tests for its detection are desirable. Those engaged in clarifying and decolorizing oils and fats are no doubt familiar with the use of Fuller's earth as a precipitant of coloring-matter, the latter usually being precipitated without any pronounced color reaction. Since text-books and the chemical literature, to my knowledge, do not mention the red to pink color which Ful-

<sup>1</sup> Read at the Washington Meeting.

ler's earth produces with some of the yellow azo dyes, I desire to call attention to the practicability of using this earth as a most convenient and delicate test for the detection of at least one, if not more, of the yellow azo dyes. The latter are now largely used as constituents of butter-colors, and replace annatto to a considerable extent.

While analyzing a sample of a reddish-colored butter intended for export, my attention was drawn to the large amount of coloring-matter present and the intense violet-red color developed when I attempted to remove the coloring-matter from the clarified fat by means of Fuller's earth. The color developed depended much upon the relative amount of Fuller's earth added, ranging from a deep violet-red to pink. All the coloring-matter giving this particular reaction was readily precipitated. The precipitate, after having been thoroughly washed with naphtha to remove the fat, presented, upon drying, a violet-red powder. Contact with alcohol immediately decolorized it, the color reappearing upon the evaporation of the alcohol. Boiling alcohol readily extracted all the coloring-matter from the precipitate, producing a yellow solution. As obtained from the latter, the coloring-matter was found to be quite insoluble in water, sparingly soluble in hot water, reprecipitating from the latter on cooling. It dissolved with a yellow color in concentrated sulphuric acid which, upon dilution with water, developed a bright pink to red color. Strong mineral acids also produced a violet to pink color. The latter reaction is familiar through the use of methyl orange as an indicator in acidimetry. True methyl orange as supplied in the market for use as an indicator, however, does not give the Fuller's earth reaction nor is it as soluble in fats as this particular coloring-matter. These reactions with others would indicate one of the yellow azo dyes. The reactions throughout corresponded closely with a commercial yellow azo dye soluble in fats and used as a constituent of butter-colors.

Applying the Fuller's earth test to various samples of butter and oleomargarine, I found a large number of the samples to give the Fuller's earth reaction even where the samples were but lightly colored.

In view of the fact that in certain localities oleomargarine was

readily sold on the strength of the statement that only "two ounces of coloring-matter had been used per ton" and that the amount was "too small to admit of detection" it became a matter of interest to determine the limit of the Fuller's earth test and the probable amount of coloring-matter present in commercial samples of average color. With this end in view mixtures were made with varying amounts of the yellow azo dye and pure white lard and the test applied to the same. The mixtures were as follows :

								Ratio.	Equivalent per ton. Ounces.
A....	100	mgms.	coloring-matter	per	kilo	of	lard	1 : 10,000	3.2
B....	50	"	"	"	"	"	"	1 : 20,000	1.6
C....	10	"	"	"	"	"	"	1 : 100,000	0.32
D....	1	"	"	"	"	"	"	1 : 1,000,000	0.032

The latter ratio indicates fourteen grains per ton. Treated with Fuller's earth

A developed a deep violet-red color,  
 B developed a deep violet-red color,  
 C developed a deep pink color, and  
 D developed a pink tint.

In the latter case a half gram of the sample spread upon a white porcelain slab developed a strong unmistakable pink upon the addition of Fuller's earth. When D was dissolved in naphtha and the Fuller's earth added to the solution, the pink appeared as a distinct ring or zone at the edge of the deposited layer of the reagent. The reaction is therefore a very delicate one.

Of the mixture A the average of several experiments showed that so minute a quantity as the  $\frac{1}{100}$  of a milligram still gave a pink reaction perceptible to the naked eye. Under the microscope the  $\frac{1}{100}$  part of this was still perceptible. Since the amount of coloring-matter actually present under the latter conditions was only  $\frac{1}{200.000.000}$  of a milligram (equivalent to  $\frac{1}{18.000.000.000}$  of a grain) the applicability of the test as a definite color reaction under ordinary conditions is apparent. The use of as little as two ounces of the coloring-matter per ton produces a highly-colored oleomargarine, while fourteen grains (the  $\frac{10}{828}$  part of two ounces) per ton would be barely perceptible as a

faint yellow tint, but readily detected by the pink tint developed by the test.

Commercially, the yellow azo dye is generally used in conjunction with an orange variety. The latter does not give the Fuller's earth test.

For practical purposes the test is readily applied by spreading some of the clarified fat to be tested upon a white porcelain surface and stirring into the fat a pinch of Fuller's earth and observing the change in color. A pink to violet-red color will appear within a few moments if any considerable proportion of this coloring-matter is present. If the experiment is performed in a glass tube it is readily preserved for court exhibits where such are desirable. The test may therefore be used as a valuable adjunct in testing for this coloring-matter in fats as well as differentiating between certain of the azo dyes.

DISCUSSION: *C. A. Crampton*.—I wish to call attention to the very valuable and *apropos* nature of this test. It seems to be a very good one and is especially valuable because this form of coloring-matter seems to have driven out of use the old-fashioned butter-color which was made of annatto. The manufacturers say the dyes "hold up" better than annatto, by which is meant, I suppose, that they will stand time and exposure to light much better. In the paper to be presented to-morrow, I hope to show some samples of this butter-color dye, which will illustrate the extent to which it is used in a certain class of butters.

*J. F. Geisler*.—It is generally claimed that these azo dyes are not detrimental to health. They are certainly used in very minute quantities.

*E. A. de Schweinitz*.—A number of physiological experiments have recently been made to determine the effect of these dyes, and, as a result, it is stated that they are not poisonous even when used in considerable quantities.

NEW YORK, DECEMBER 20, 1897.

## THE LECITHINS OF SUGAR-CANE.

BY EDMUND C. SHOREY.

Received November 23, 1897.

IN a former paper on the principal amid of sugar-cane, mention was made of an attempt to estimate the amount of different nitrogenous bodies in molasses, according to a scheme by

which the albuminoids were precipitated by cupric hydroxide, and the nitrogen in the precipitate, produced in the filtrate from the cupric hydroxide by phosphotungstic acid, was designated peptones. The reagent used was a solution of sodium phosphotungstate in dilute sulphuric acid, and this was added to the filtrate from the cupric hydroxide precipitate, previously rendered strongly acid by sulphuric acid. I found that, so used, this reagent produced a copious precipitate in raw cane juice, and in the after products of the sugar house, clarified juice, syrup, and molasses. The precipitate so formed was flocculent and easily washed by decantation, chocolate in color, and varying very little in its character with the source from which it was obtained. This precipitate I found invariably contained nitrogen; *e. g.*, a typical sample of raw cane juice gave, according to this scheme of analysis, the following figures:

	Weight of juice. Per cent.
Total nitrogen.....	0.034
Nitrogen in cupric hydroxide precipitate .....	0.023
Nitrogen in phosphotungstic acid precipitate.....	0.005

In attempting to determine the character of the nitrogenous compound thus precipitated by phosphotungstic acid, I at first adopted the usual method of decomposing this precipitate by digesting with barium hydroxide or carbonate, or milk of lime. By this method I found that salts of a fatty acid were invariably formed, and in order to isolate the body from which the fatty acids were evidently formed by decomposition, I adopted the following method. The precipitate produced by phosphotungstate of sodium, after being well washed by a solution of the precipitant, was nearly dried over sulphuric acid at the temperature of the laboratory, mixed to a paste with dry sodium carbonate, and extracted with ninety per cent. alcohol; which resulted in a dark red solution. The alcohol was removed by distilling in a vacuum, and the residue taken up with a small quantity of water. The watery solution, which was dark red and turbid, was agitated several times with ether. The resulting ethereal solution was light yellow in color, and after evaporation of the ether there was left a light yellow, translucent, wax-like solid, with all the physical properties of the lecithins, containing



nitrogen and phosphorus, and decomposing by alkalies into fatty acids, glycerophosphoric acid, and an alkaloid or alkaloids.

Sugar-cane lecithin was proved to give more than one fatty acid, on decomposition, by the following method: The barium salts obtained by digesting the lecithin with barium hydroxide were decomposed by sulphuric acid, the free fatty acids separated and precipitated by lead acetate. The resulting lead salts were agitated with ether, when a portion was dissolved, and from the portion so dissolved free oleic acid was obtained. From the portion of lead salts insoluble in ether free fatty acids were obtained which were solid at the ordinary temperature with a melting-point of  $65^{\circ}$  C.; probably a mixture of palmitic and stearic acids. It is thus shown that the lecithin of sugar-cane is a mixture of several lecithins. Schulze and Likiernik have shown this to be the case with the lecithin of vetch and lupin seeds.<sup>1</sup>

I have not yet determined the proportions of different fatty acids yielded by any sample of sugar-cane lecithin.

The alkaloid body resulting from the decomposition of sugar-cane lecithin by barium hydroxide I found to be a mixture of betaine and choline. In separating these bodies the method of Schulze and Frankfurt<sup>2</sup> was followed. The precipitate obtained with phosphotungstic acid was treated in the cold with milk of lime, filtered, excess of lime precipitated as carbonate, and the solution neutralized with hydrochloric acid, evaporated nearly to dryness, and extracted with ninety per cent. alcohol. To this solution an alcoholic solution of mercuric chloride was added, and after several days the double chlorides of mercury and the alkaloids which had been thrown down were removed and decomposed by hydrogen sulphide. The resulting hydrochlorides, on treatment with absolute alcohol, were separated into a soluble and an insoluble portion, proving the presence of both choline and betaine. From the soluble portion choline platinichloride, containing 10.2 per cent. platinum, was prepared.

Whether choline and betaine exist in sugar-cane in a free condition, or whether they have been obtained wholly as decomposition products of lecithin, I am as yet not prepared to say.

<sup>1</sup> *Ber. d. chem. Ges.*, 24, 71.

<sup>2</sup> *Ibid.*, 26, 2151-2155.

The usual method of estimating lecithin is to convert the phosphorus contained therein into phosphoric acid by fusion with carbonate of sodium and potassium or with sodium carbonate and potassium nitrate, and determination of the phosphoric acid in the usual way by precipitation with ammonium molybdate and magnesia mixture, and calculating to lecithin from the known per cent. of phosphorus: distearyl lecithin containing 8.798 per cent., phosphorus pentoxide being taken as the type.

The lecithin obtained in the manner already described from a number of samples of raw cane juice, and the phosphorus pentoxide estimated in the usual manner, gave, using the factor for distearyl lecithin, a quantity of lecithin representing a much less quantity of nitrogen than was contained in the phosphotungstic acid precipitate. Of the two conclusions to be drawn from this—that there were other nitrogenous bodies in the precipitate, or that the lecithin was imperfectly separated by the method used—both are true. I have always found the residue from the extraction with ether to contain nitrogen, but I have not yet been able to determine the nature of the body in question. A large portion of the phosphotungstic acid precipitate is made up of a coloring-matter of a glucosidal nature, free from nitrogen.

In itself, there is nothing noteworthy in the isolation of lecithin from sugar-cane any more than there would be in proving the presence of an amid in this plant or any other vegetable product; for it is generally believed that lecithins like the amids are normal constituents of all plants during some period of their growth. In this instance there are, however, several points connected with the manner of its isolation, which are of interest to the analyst.

It has been customary with some chemists in stating the analyses of the nitrogenous constituents of plants free from alkaloids, to give the total and albuminoid nitrogen actually determined, and to designate the difference between these as amid nitrogen. This plan has often been adopted in stating analyses of sugar-cane, and I have several times published analyses of cane according to this method. The error of this is seen on referring to the analysis already given, in which the difference between the total and albuminoid nitrogen is 0.011 per cent. This would ordinarily be designated amid nitrogen, but phos-

photungstic acid, which we know does not precipitate amids, precipitates 0.005 per cent. nitrogen, leaving only 0.006 per cent. as possible amid nitrogen. In some samples of juice I have found that this error would be much greater; *e. g.*, a sample of raw juice gave :

	Per cent.
Total nitrogen.....	0.033
Albuminoid nitrogen .....	0.018
Nitrogen precipitated by phosphotungstic acid.....	0.014

leaving a difference of only 0.001 per cent. as possible amid nitrogen, which according to the plan usually adopted would be stated as 0.015 per cent.

Again, the designation of the nitrogen in the phosphotungstic acid precipitated as peptones, is in the case of sugar-cane erroneous. I have repeatedly examined this precipitate for peptone nitrogen and have found none; and if such nitrogen exists in mature cane it must be very small in amount.

The ease with which lecithin breaks up on treatment with alkalies should be kept in mind by the analyst if he is to ascertain what bodies actually exist in the plant examined. No doubt in many cases, when choline and betaine have been reported as present in plant products, they have been present not as such but in the form of lecithin, which has been broken up in the course of analysis.

To the physiologist lecithin is one of the most interesting and important compounds. The rôle of phosphoric acid in plant growth and the connection of lecithin therewith is an obscure one, and although sugar-cane responds freely to phosphoric acid fertilizers, it seems to me that the part which lecithin plays in plant life can be more advantageously studied in connection with other plants of quicker growth and containing smaller amounts of soluble carbohydrates.

To the sugar manufacturer the presence or absence of lecithin in cane juice can, owing to the small amount ever present, make very little difference, either in the working of the juice or in the yield of sugar obtained.

It is a property of lecithin to be precipitated with other precipitates when it would not be precipitated alone, so that it is probably partially removed from cane juice in clarification. I

have, however, obtained lecithin from refuse molasses, showing that part, at least, of that originally present in the juice had escaped precipitation and decomposition during the treatment of the juice in the sugar house.

The ease with which lecithin is decomposed has suggested one point of interest to the sugar manufacturer. Cane juice is generally concentrated to a syrup in a multiple effect evaporator, the first cell of which is heated by exhaust steam from the engines; the second and succeeding cells are heated by steam from the boiling juice in the preceding cell. The inner or steam side of the drums or coils of these cells soon becomes coated with grease which, if not removed by treatment with alkali, lessens the efficiency of the evaporator. The grease in the first cell is, of course, derived from the oil in the exhaust steam, but that in the second and succeeding cells can be derived only from the boiling juice. It no doubt is derived in part from fats and wax naturally occurring in sugar-cane, but also no doubt due in part to the decomposition of lecithin and the carrying over of the freed fatty acids with the steam. This decomposition takes place slowly in boiling neutral solution; in alkaline solution it is very rapid.

The work done so far on the lecithins of sugar-cane, outlined above, I regard as preliminary, and have in view the following objective points :

1. A more accurate determination of the lecithin present in mature cane supplemented by determinations of the amounts in cane at different stages of growth.

2. An accurate determination of the amounts and kinds of fatty acids yielded by sugar-cane lecithin and thus indirectly the amounts of different lecithins.

3. An estimation of the amounts of choline and betaine in mature cane and a decision as to whether they ever exist free or are only obtained as decomposition products of lecithin.

[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, No. 7]  
**A REVISION OF THE ATOMIC WEIGHT OF ZIRCONIUM.<sup>1</sup>**

BY F. P. VENABLE.

Received January 6, 1898.

I. PURIFICATION OF THE MATERIAL.

**P**REPARATORY to entering upon the revision of the atomic weight of zirconium, a study was first made of the best method of decomposing zircons and securing pure preparations.<sup>2</sup> The pulverized zircons were fused in nickel crucibles with sodium hydroxide and sodium fluoride. The melt was washed, dissolved in hydrochloric acid and filtered from some of the silica and from undecomposed zircon. This filtrate was evaporated to dryness to render the silica insoluble, again dissolved in diluted hydrochloric acid and filtered, and this was repeated two or three times. The further purification consisted in precipitation by ammonium hydroxide, washing, and re-solution in hydrochloric acid, followed by repeated crystallizations from boiling concentrated hydrochloric acid. After it had been thus purified it was found that traces of silica were still present. To remove these, the chloride was dried, ignited, and the powdered zirconia was again and again treated with hydrofluoric acid. After driving this off the zirconia was again melted with potassium hydroxide (purified by alcohol), taken up with hydrochloric acid and subjected once more to crystallization from strong hydrochloric acid. These crystallizations varied in number from twenty to thirty odd, and if those which preceded the second fusion are to be taken into account, exceeded sixty in all. Just before using in the series of determinations of the atomic weight, this purified chloride was filtered by means of an unglazed porcelain suction filter which had been cleaned by boiling for several days in strong hydrochloric acid and then standing three days in fresh cold hydrochloric acid. The last acid was entirely free from color. This filter was kept under distilled water when not in use. The filtration had to be carried out with hot solutions, but the liquid was not in contact with the filter more than five or six minutes.

When this work was undertaken it was believed that the substance under examination was zirconium tetrachloride. This

<sup>1</sup> Read at the Washington Meeting.

<sup>2</sup> *J. Anal. Appl. Chem.*, 5, 551-554.

belief was based on the work of Linnemann and upon my own determinations of the zirconia, these agreeing fairly well with the amount required for  $\text{ZrCl}_4$ . At the close of the determinations of zirconia recorded later, some determinations of the chlorine present were made and were found not to agree at all with the amount requisite for the supposed formula. The matter did not seem easy of explanation, and the work was laid aside until time could be gotten for a more thorough study of this body. My study of the oxychlorides of zirconium has shown that there are at least three :

$\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  when crystallized from strong hydrochloric acid.

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  when crystallized from water.

$\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$  when precipitated by hydrochloric acid from an aqueous solution.

All of these, dried in a stream of hydrogen chloride at  $100^\circ$ – $125^\circ$ , have the formula  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$ , and this water is lost only by heating from  $180^\circ$  to  $210^\circ$ .

The liquid filtered as above is clear and bright and soon begins to deposit groups of needle-like crystals, or it crystallizes to a solid mass if a large amount of the salt is present. In several cases the crystallization was repeated two or three times from acid after this filtration, but no perceptible difference was made in the results. These crystals take up a considerable amount of acid which cannot be drained off. In this acid they easily melt, and if the excess is removed under a stream of hydrochloric acid gas the chloride can be gotten in the form of a dry white powder. The oxychloride can be thus dried without decomposition under a stream of hydrochloric acid gas at the temperature of  $100^\circ$ – $125^\circ$  C. to  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$ . As the difficulty in drying this salt was the main stumbling block in the way of previous workers, interfering with its use for atomic-weight work, the removal of this obstacle seemed to place it among the most suitable of the compounds to be used for the purpose. A full account of the examination of the chlorides will be published shortly. Other compounds have been examined also in the progress of this work, and though they may be used hereafter, they have seemed to me to present more difficulties than the chloride, and so this has been taken first.

## PREVIOUS DETERMINATIONS OF THE ATOMIC WEIGHT.

It is perhaps best to give here a brief outline of previous determinations of the atomic weight of zirconium. Six such series have come under my notice. In three of these the sulphate was used, and in the others the chloride and the double fluoride of zirconium and potassium were used, and in one the selenate.

The determinations of Hermann,<sup>1</sup> by means of the chloride, can be dismissed as untrustworthy, because of his failure to overcome the difficulties inherent in the use of the chloride as shown by Bailey's work and my own.

The work of Marignac upon the double fluoride I am not in a position to criticise properly, except in so far as to say that his analyses are not very numerous, and that they show a range of nearly three units in the atomic weight.

In 1825 Berzelius ignited the sulphate and gave six determinations of the ratio of the sulphate to the oxide. In some of the experiments he also precipitated the zirconium hydroxide by means of ammonium hydroxide and determined the sulphuric acid in the filtrate by precipitation with barium chloride.

Mats Weibull also used the sulphate and reports seven experiments with an entire consumption of 8.2335 grams. Bailey's own determinations number eight, using in all more than sixteen grams. He gives full data as to his work, and it is well done and merits very careful attention. The following table is copied from his article.<sup>2</sup> The figures have been recalculated to the basis of  $O = 16$ .

	Mean.	Maximum.	Minimum.	
Zr : Cl	88.77	....	....	Hermann
ZrO <sub>2</sub> : HCl	90.14	90.98	89.29	Hermann
K <sub>2</sub> ZrF <sub>6</sub> : K <sub>2</sub> SO <sub>4</sub>	90.53	92.80	90.06	Marignac
ZrO <sub>2</sub> : K <sub>2</sub> SO <sub>4</sub>	90.64	91.26	90.24	Marignac
K <sub>2</sub> ZrF <sub>6</sub> : ZrO <sub>2</sub>	90.8	91.3	89.9	Marignac
Zr(SO <sub>4</sub> ) <sub>2</sub> : ZrO <sub>2</sub>	89.45	92.65	89.27	Berzelius
Zr(SO <sub>4</sub> ) <sub>2</sub> : ZrO <sub>2</sub>	89.48	90.38	89.13	Mats Weibull
Zr(SO <sub>4</sub> ) <sub>2</sub> : ZrO <sub>2</sub>	90.65	90.78	90.46	Bailey

It is manifest that the determinations based upon the ignition of the sulphate are the only ones worthy of further attention. A

<sup>1</sup> *J. prakt. Chem.*, 31, 77.

<sup>2</sup> *Chem. News*, 60, 17.

brief criticism of these is necessary. First, as to Mats Weibull, Bailey says that the temperature used by him in freeing the sulphate from the excess of sulphuric acid was some  $50^{\circ}$  too low. This would of course give him variable and low results. Berzelius does not give exact data as to temperature used, but he seems to have heated the sulphate too high in driving off the excess of acid. Possibly more stress is to be laid upon the question of the purity of his sulphate and the correctness of the assumption that he had in hand the normal sulphate.

Bailey concludes from his experiments that the sulphate is stable up to  $400^{\circ}$  C., and that the excess of sulphuric acid can be completely driven off by the use of a temperature between this and  $350^{\circ}$  C. He further states that a mixture of the salt and free acid, as prepared by him, when heated to this temperature until constant, yields the normal sulphate. It must be said that he gives no proofs of this beyond the amount of zirconia found in his atomic weight determinations.

Whilst certain criticisms of the work of Bailey have occurred to me, I will refrain from mentioning them until I have had opportunity to repeat his experiments and so make myself more familiar with the details of his method.

One criticism I can venture upon now, however. I doubt whether it is possible to ignite, without loss, zirconia along with ammonium carbonate, as was done by Berzelius and by Bailey to remove the "last two or three milligrams of sulphuric acid." I have not ventured to use this method in getting rid of the chlorine which is held just as tenaciously as the sulphuric acid, as I feel sure that it could not be done without loss. Bailey adopted extraordinary precautions to prevent this loss, but it seems to me that it is not the currents of the external atmosphere, as he maintains, which are to be most avoided, but the mass of escaping vapor of the ammonium salts. It is easily possible for him to have lost several milligrams of the finely-divided zirconia in his way, and as he states, each milligram was equivalent to a variation of 0.25 in the atomic weight.

#### THE WEIGHINGS.

In the following experiments the amounts of substance used varied from one to five grams. To avoid the disadvantage of a



small error causing a large variation in the result, I would gladly have used larger amounts of the chloride, but many difficulties met me there. The purification of the zirconium chloride is slow and costly. It is best carried out in small portions of a few grams at a time. Some fifty grams have constituted the stock at my command. The drying of large portions and the subsequent ignition would be exceedingly tedious and time consuming, besides requiring such apparatus as could not be well afforded. Five or six grams have been about the largest amounts that could be well handled at one time. Even such an amount as that required from sixteen to twenty days for the completion of the experiment. It could not safely be hurried through in shorter time.

The weighings were carried out upon an excellently constructed Sartorius balance, intended for a load of 200 grams. The heaviest apparatus used weighed less than sixty grams. The weights were corrected by one which had been compared with the standard at Washington. All objects were weighed against a tare of as nearly the same size, form, and weight as possible, all of the flasks, crucibles, etc., being made in pairs. This partly avoided the necessity for a reduction of the weighings to a vacuum and corrections for moisture, pressure, etc. Such corrections would have had little meaning in comparison with the other inaccuracies of the process and manipulation, and could only serve to give a false appearance of excessive accuracy. The objects were left one-half hour in the balance-case before weighing, experiments having shown that this time was sufficient. Of course the adjustment of the balance was carefully watched, and the balance, which has been used very little, was put to no other use during the progress of these experiments.

#### METHOD OF WORK.

The purified chloride was introduced into a small glass flask having a capacity of 100 cc. This was provided with a glass stopper ground to fit, and also a second one with two tubes arranged for the passage of the hydrochloric acid gas. The arrangement of the tubes was similar to that in an ordinary ether wash-bottle, though both tubes outside were bent down-

wards and had little bulbs blown in them for catching moisture, etc. A Thörner bath was found to be very convenient for keeping these flasks at  $100^{\circ}$  C. The hydrochloric acid was prepared by allowing sulphuric acid to drop into a large flask containing the hydrochloric acid. The gas thus obtained in a regular stream, was passed through a wash-bottle containing sulphuric acid and then through towers filled with glass beads kept moist with concentrated sulphuric acid.

The drying took from fifty to one hundred hours (in some extreme cases). If the stream of gas was rapid the temperature could rise to  $110^{\circ}$  or even higher without decomposition of the chlorine. A much lower temperature caused this decomposition if the stream was insufficient to keep the flask full of gas. A number of experiments were carried out showing these facts. Indeed, two in the series of determinations were lost by the stream of gas becoming too slow or altogether ceasing for a short while. (Experiments VI and VIII.) It was thought from experiments at first that where this decomposition had begun it was impossible to secure a constant weight of the residue, but this is certainly not true where the decomposition has been only slight. Of course this introduces a chance for error in the method. The drying must be watched quite closely, and not more than eight or ten hours of drying could be easily managed in a day.

At first it was feared to remove the atmosphere preparatory to weighing, and efforts were made at weighing the flasks full of hydrogen chloride. These results were too low and varied among themselves, so that it was evidently impracticable to carry out the experiments in this way. It was found that the hydrochloric acid could be replaced by dry air. The flask was removed from the bath and dry, pure air passed through it for half an hour. It is of course essential that the air be carefully dried. The tubes are then removed and the glass stopper quickly fitted in its place. It is then ready for placing in the balance-case. The chloride is deliquescent and some trouble in weighing was experienced. If the stopper was well ground there was no appreciable change in the weight in from twenty to forty minutes after placing upon the balance. The loss of weight in the latter part of the drying was very slow. The weighings were taken at intervals of from six to eight hours' heating. The num-

ber of weighings necessary before constancy was secured served as a safeguard against error. A series of such weighings is given further on.

After drying, the chloride was dissolved in a small amount of water (redistilled) and this solution, with rinsings, transferred to a platinum crucible. It was evaporated to dryness upon a water-bath, with due precautions against dust, etc., was next heated gradually upon a sand-bath until most of the chlorine had been driven off, and was then slowly raised to the highest temperature attainable by the Bunsen burner. During this latter part of the operation the cover was kept on. Three or four days were thus consumed, the gradual heating giving a coherent flinty mass of glistening semi-translucency which could be safely heated by the water-blast without loss. During the driving off of the chlorine the platinum crucible was more or less attacked, but as this was before the lid was on, there was little chance of loss from this source. This corroded platinum was probably the reddish-brown decomposition product mentioned by Bailey as coming from the ignition of the oxychloride.

The last of the chlorine was driven off by heating with a water-blast for from forty-five to seventy hours. The last weighings were made at intervals of from six to twenty hours and were recorded as constant if they agreed within 0.00005 of a gram. A series of weighings is here given as an example. Experiment No. II, or the first one successfully carried out in the series, is taken for the purpose.

Weights of zirconium chloride: March 28.....						5.25910
"	"	"	"	"	29.....	5.25786
"	"	"	"	"	30.....	5.25760
"	"	"	"	April 1.....		5.25762
Weights of zirconium oxide: April 11.....						2.78759
"	"	"	"	"	12.....	2.78724
"	"	"	"	"	13 .....	2.78583
"	"	"	"	"	15.....	2.78517
"	"	"	"	"	16.....	2.78452
"	"	"	"	"	17.....	2.78451

This zirconia was examined for chlorine in most of the analyses and was found to be free from it. In the last three experiments reported in the series, the ignited residue was treated with

hydrofluoric acid. Ignition after this treatment was very difficult, as the mass was not compact and coherent. The finely divided zirconia was lost in spite of the most careful treatment. The first was lost altogether and the weighing was not carried out. The second showed, upon the lid signs of the powdered zirconia having been swept out. The total loss of weight, however, was less than one milligram. This could readily be attributed to the zirconia and pointed to the absence of silica unless in insignificant traces.

I think great purity may be claimed for the preparations used in the analyses. Crystallizing from hot hydrochloric acid is apt to remove most known impurities, and they were eliminated beyond the possibility of detection by the ordinary tests. The analyses were not made from the same preparation, but from small quantities prepared at different times and some crystallized ten or a dozen times more than others, yet no appreciable difference could be detected in the results. That these results are not in close accord with one another, is due in part to the deliquescence of the chloride and to the risks involved in the prolonged heating of the oxide.

#### SOURCES OF ERROR.

Five main sources of error have occurred to me apart from any question as to the purity of the material.

1. The deliquescence of the chloride.
2. The loss of the finely divided zirconia.
3. The corrosion of the platinum crucibles.
4. The attack of the glass flasks by the gaseous and liquid hydrochloric acid. It is very evident that the glass vessels would suffer when subjected to the action of hydrochloric acid during such prolonged periods. The weighings easily revealed the extent of this action. It was found to vary with different flasks. For instance, flask I lost 0.00116, 0.00031, 0.00023, and 0.00078 gram. On the other hand, flask IV weighed after the first experiment only 0.00011 gram less, and after the next two experiments the loss was 0.00013, and the total loss during three experiments was 0.00024. This is probably transferred mainly as alkaline chlorides to the crucibles and is there volatilized. Sodium could readily be detected upon the lid of the crucible

after partial ignition. Of course if all is volatilized then no error is introduced into the experiment, but there may be some non-volatile material also transferred from the flasks. The total amount is so small that the error cannot be a large one.

5. Substances carried into the drying flasks by the stream of gas. Much care was taken to avoid error from this source. The main danger lay in the necessity for the use of some rubber connections. Vulcanized rubber was used. It was freed from excess of sulphur and was replaced by fresh pieces when attacked by the gas. The dry gas does not attack rubber very rapidly. Gaseous sulphur compounds, coming from the sulphuric acid, used in preparing and drying the hydrogen chloride, were probably carried through the drying flasks, but there seems to be no probability of their causing a decomposition of the oxychloride.

#### THE DETERMINATIONS.

All analyses which were completed under the proper conditions of the method, as already given, are here reported. Experiment III became contaminated from the iron support during the prolonged heating and came out consequently a little high, giving the ratio of  $\text{ZrO}_2 : \text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$  as 53.12. In most of the subsequent analyses the ignition was carried out with the crucible suspended in a platinum wire cage from a glass support. Experiments VI and VIII were dried with an insufficient stream of gas, as already stated, and hence were partially decomposed. They gave 53.57 and 53.8, respectively. The remaining analyses follow :

	$\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$	$\text{ZrO}_2$	Ratio.
II.....	5.25762	2.78450	52.961
IV.....	3.53994	1.87550	52.981
V.....	3.25036	1.72435	53.051
VII.....	1.52245	0.80708	53.012
IX.....	2.98802	1.58274	52.969
X.....	2.11371	1.11920	52.949
XI.....	2.38139	1.26161	52.978
XII.....	1.90285	1.00958	53.055
XIII.....	2.61847	1.38658	52.954
XIV.....	1.07347	0.56840	52.951
	<hr/> 26.64828	<hr/> 14.11953	<hr/> 52.986

Calculating these for the ratio  $Z:OCl_2:3H_2O : Z:O_2$ , taking  $H = 1.008$ ,  $O = 16$ , and  $Cl = 35.45$ , we have the following:

MAXIMUM	.....	53.555	Atomic weight.....	91.12
Mean	"	52.986	"	90.78
MINIMUM	"	52.567	"	90.61

The atomic weight as determined by Bailey is 90.65. The mean value given in Clarke's Recalculation is 90.40. I purpose repeating the determinations with the oxychloride, with such modifications as have occurred to me since the completion of the above work.

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## THE SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF OXALIC, TARTARIC, AND CITRIC ACIDS.

By C. E. LIVERGIER

Received January 5, 1912

IN the determination of the surface-tensions of the solutions of citric, oxalic, and tartaric acids, the apparatus described in a previous number of this Journal<sup>1</sup> was employed. The "apparatus constant" was ascertained directly before and after a series of determinations, Ramsay and Shields'<sup>2</sup> data for water being taken as the standard; the variation, when there was one, which seldom happened, affected only the decimal places after the second. At least five readings of the adjustment of the tubes were made for every solution, and their average taken. The specific gravity of the solutions were determined to one or two figures in the fourth decimal place and were referred to water at temperature of its maximum density.

The thermometer had been tested by the Physikalische Reichsanstalt, at Berlin, and found to be without appreciable error in the neighborhood of 20°.

The acids were the purest obtainable and were recrystallized once or twice.

The solutions were prepared by dissolving the solid acids so as to form almost saturated solutions, and then diluting this stock solution; their surface-tensions were measured very soon after they were made up, although it was found that that phys-

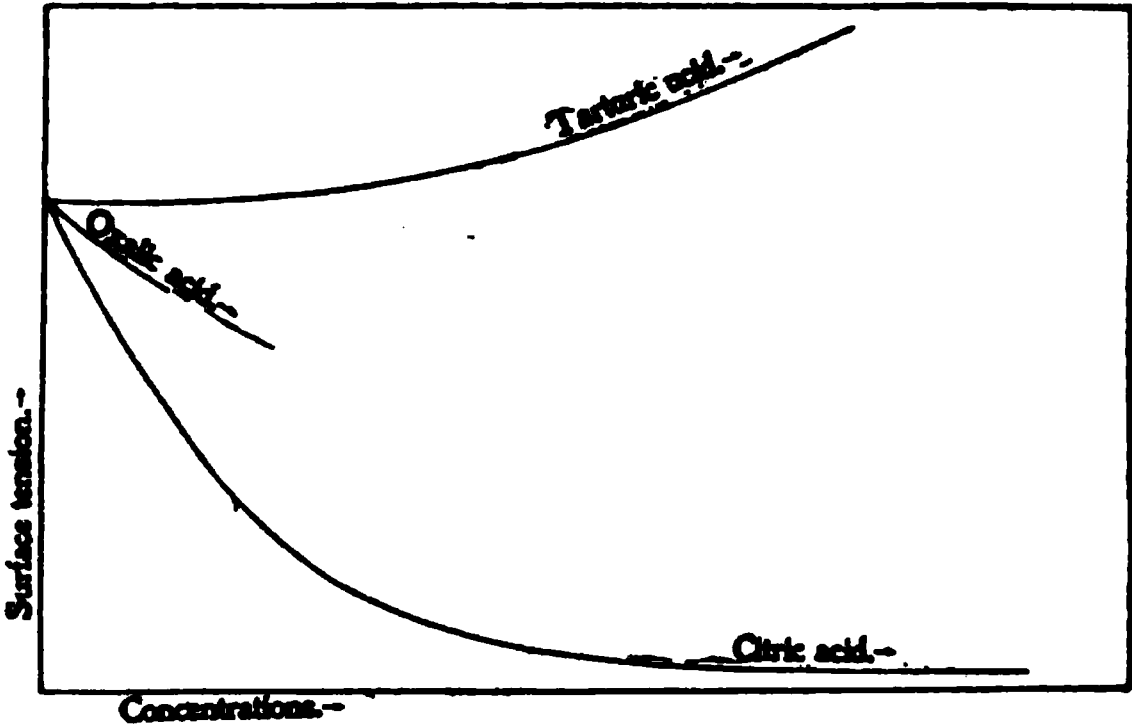
<sup>1</sup> This Journal, 18, 514.

<sup>2</sup> *Ztschr. phys. Chem.*, 12, 471. Surface-tension for water at 15° was taken to be 71.27 dynes per cm.

ical property did not alter with time, provided the solutions were hindered from evaporation; enough solutions to clearly determine the curve for each acid were investigated.

The percentage composition of the solutions were taken from the tables of specific gravities prepared by Gerlach.

The following tables contain the data which are represented graphically in Fig. 1; the curve for oxalic acid is raised a little



so as to make its origin coincide with the origin of the other curves; this slight shift has no appreciable influence on the shape of the curve.

SURFACE-TENSION OF OXALIC ACID SOLUTIONS AT 17.5°.

Per cent. acid.	Apparatus constant.	Specific gravity referred to water at 4°.	Distance between ends of tubes.	Surface-tension in dynes per cm.
1.53	1.275	1.0087	54.15	70.65
2.91	1.275	1.0152	53.71	70.55
4.33	1.275	1.0243	53.21	70.34
9.13	1.275	1.0323	52.25	69.85

SURFACE-TENSION OF TARTARIC ACID SOLUTIONS AT 15°.

18.18	1.278	1.0870	50.57	71.44
33.33	1.278	1.1866	46.75	72.11
50.05	1.278	1.2699	44.23	73.39
53.32	1.278	1.2913	43.74	73.86

SURFACE-TENSION OF CITRIC ACID SOLUTIONS AT 15°.

6.12	1.268	1.0223	52.70	69.35
8.03	1.268	1.0313	51.89	68.91
18.05	1.268	1.0708	47.97	66.27
29.96	1.268	1.1243	45.07	65.46
31.11	1.268	1.1301	44.72	65.41
43.52	1.268	1.1865	42.34	65.17
58.00	1.268	1.2656	39.62	65.19
64.53	1.268	1.2990	38.55	65.18
65.08	1.268	1.3011	38.50	65.19

The curves are quite different in trend. Oxalic and citric acids diminish in surface-tension as the concentration increases; the limited solubility of oxalic acid does not permit of an extended comparison of the two acids, however. A curious fact about the curve for citric acid is its being rectilinear and parallel to the  $x$ -axis at concentrations varying between thirty-five and sixty-five per cent.; within this range the surface-tensions of the solutions are independent of their concentrations.

The curve for tartaric acid gradually rises, becoming steeper and steeper as the concentration increases. For moderate concentrations it is approximately straight, which, for that matter, is the case with the other two acids also.

The reasons for the peculiarities of these curves are probably to be sought in the possible molecular polymerization and undoubted electrolytic dissociation of the acids in aqueous solution; very complicated relationships are presented, which in the absence of other physical data on the subject, it would now be unprofitable to attempt to unravel.

## SODIUM PEROXIDE IN QUANTITATIVE ANALYSIS.<sup>1</sup>

BY C. GLASER.

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WHEMPEL<sup>2</sup> and J. Clark<sup>3</sup> first proposed to use sodium peroxide in quantitative analysis. Hempel employed it for the oxidation of chromium, manganese, tungsten, and tin, and subsequent determination by known means; he also mentions that sulphur is completely oxidized to trioxide. He further recommends the reagent for the decomposition of zinc-blende and galena.

J. Clark recommends it for the estimation of sulphur, arsenic, and chromium, also for the separation of manganese from zinc, nickel, and cobalt. He states<sup>4</sup> that the action of sodium peroxide on coke and coal is too violent for analytical purposes. T. Spüller and S. Kalman<sup>5</sup> use it on ferrochrome, chrome steel,

<sup>1</sup> A review of various propositions made since 1892.

<sup>2</sup> *Zentr. anorg. Chem.*, 1892, 2, 193-194.

<sup>3</sup> *J. Chem. Soc.*, 1893, 2779.

<sup>4</sup> *Ibid.*, 69, 2779.

<sup>5</sup> *Chem. Ztg.*, 17, 21.



chrome iron, and also sulphurets. Poleck<sup>1</sup> experimented on organic substances, as did J. Tafel.<sup>2</sup>

In 1894, M. Hoehnel and C. Glaser<sup>3</sup> made revised recommendations for the estimation of sulphur in pyrites. O. Kassner<sup>4</sup> states that iron is precipitated as hydroxide, but not changed into ferric acid, that, on the contrary, solutions of ferric acid are reduced by sodium peroxide. He gives detailed statements concerning separation of chromium and manganese; of the decomposition of freshly precipitated sulphides of antimony, tin, and arsenic. In 1895, L. Archbutt<sup>5</sup> reports an analysis of sodium peroxide, showing the presence of nearly one-half of one per cent. of iron and alumina in the commercial article. Alb. Edinger<sup>6</sup> gives his experience in the determination of sulphur and chlorine in inorganic and organic combinations. M. C. Schuyler<sup>7</sup> proposed to determine mercury in mercuric salts by reduction to metal with sodium peroxide. In 1897 S. W. Parr<sup>8</sup> reports on the adaptability of sodium peroxide as a third group reagent in qualitative analysis, practically a review of the above-named publications, omitting quantitative features.

The *Chemiker Zeitung*<sup>9</sup> contains a second note of the author, suggesting some improvements in the determination of sulphur in pyrites and later the same author<sup>10</sup> separated iron from aluminum in phosphates and other minerals by means of sodium peroxide.

It may be in place here to state that the C. P. sodium peroxide of the trade has, as far as I have had occasion to test it, proved quite free from oxide of iron and alumina. It appears therefore probable that the article analyzed by Archbutt was a crude commercial product.

I cannot confirm O. Kassner's statement, that iron is not oxidized to ferric acid by sodium peroxide. If the reagent is added to a solution of an iron salt, without the precaution of

<sup>1</sup> *Chem. Ztg.*, 18, 103.

<sup>2</sup> *Ber. d. chem. Ges.*, 27, 816.

<sup>3</sup> *Arch. Pharm.*, 232, 222; *Chem. Ztg.*, 18, 1448.

<sup>4</sup> *Arch. Pharm.*, 232, 226.

<sup>5</sup> *Analyst*, 20.

<sup>6</sup> *Ztschr. anal. Chem.*, 34, 362.

<sup>7</sup> *Chem. Ztg.*, 20, 1896.

<sup>8</sup> This Journal, 19, 341.

<sup>9</sup> *Chem. Ztg.*, 21, No. 6.

<sup>10</sup> *Ibid*, 21, No. 69.

keeping the temperature of the latter sufficiently low, his statement holds good. But if this last condition is complied with by keeping the solution comparatively cool, a sufficient excess of the reagent will produce a perfect solution, as I have stated in the above, last-named paper.

I desire especially to recur to J. Clark's statement that the action of sodium peroxide on coke and coal is too violent to permit of use in analysis. I have used this reagent in a considerable number of coke, coal, and asphalt analyses for sulphur with perfect success, and I now present a short description of the method as I carry it out.

The material to be analyzed is placed in a sufficiently large silver or nickel dish and covered with about four times its weight of sodium carbonate. Upon this a piece of sodium hydroxide is laid, about one half the weight of the carbonate used.

The dish is now moved carefully and slowly over a small flame until the gas generation subsides and a half-fused mass is obtained. Upon this mass dry sodium peroxide is now dusted from a porcelain or platinum spoon in small quantities at a time, always waiting until the reaction is over. This is continued until all carbon is burned away, when the mass, if necessary, is heated to perfect fusion. Usually this is obtained by the heat generated by the combustion in the dish, which, however, takes place so quietly, that no loss by explosion or spurting will occur. After this operation the determination of sulphur is carried to an end in the well-known way.

I believe that this method will prove quite a relief to those chemists, who have to make many sulphur determinations in coke and coal, and who know the uncertain working of a fusion with potassium nitrate. At least it has been my experience that it is difficult to so regulate the temperature of the fusion as to avoid explosion with loss. Even the use of double crucibles has not always proved successful. The time required for the operation with sodium peroxide is quite short; with coke about five minutes, with coal probably ten, while with asphalt, owing to the peculiar nature of the material, it will take a little longer.

In analysis of chrome ores sodium peroxide does not appear to fulfil the hopes of those chemists who first proposed it. The oxidation is reported to be never perfect in one operation, which

makes the method more complicated and troublesome than a fusion with potassium nitrate and borax.

This was to be expected, since even chromic salts in solution require more than one treatment with sodium peroxide before complete oxidation to chromic acid is effected.

With this exception sodium peroxide has proved a very useful and convenient reagent, applicable in a great number and variety of cases. It ought to be, and no doubt will become, one of the standard reagents of a modern laboratory.

BALTIMORE, DECEMBER 7, 1897.

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### ADDITIONAL NOTES ON THE SUGAR-CANE AMID.

BY EDMUND C. SHOREY.

Received January 8, 1898.

**I**N a paper on the principal amid of sugar-cane, which appeared in this Journal, November, 1897, I gave the result of work done during the last grinding season on the amid present in sugar-cane. Since then I have been able to correct some errors in the work done then, and have also obtained additional proof of the correctness of the conclusion reached that this amid is amidoacetic acid and not asparagin.

The chief error in my former work which I wish to correct now, was with respect to water of crystallization. In the first examination of the crystallized sugar-cane amid it was found that the crystals, when well dried by pressing between filter-paper, did not lose weight during a short exposure to a temperature of 100° C. Subsequently it was found that the crystals, when finely powdered, lost water at 105°–110° C., and the average of several determinations, drying until there was no further loss in weight, gave 10.72 per cent. This, if we accept the formula  $\text{CH}_3\text{NH}_2\text{COOH}$  as representing the molecule of glycocoll, is equivalent to half a molecule of water of crystallization. This was discovered too late to correct the error in my first paper.

The samples in which nitrogen was determined were in all cases finely powdered and dried at 110° C. so that 18.69, the per cent. of nitrogen stated, is that present in the amid after water of crystallization has been driven off.

The presence of water of crystallization in the sugar-cane amid of course invalidates my statement that it contains the

same amount of nitrogen as asparagin: asparagin with one molecule of water of crystallization containing 18.66 per cent., while the sugar-cane amid with half a molecule contains 16.6 per cent. nitrogen. I have recently made some determinations of the nitrogen in this amid, taking large clear crystals and drying merely by pressure between filter-paper. The average of four such determinations was 16.58 per cent. nitrogen.

In concentrating the filtrate from mercuric sulphide there is sometimes deposited, before crystallization of the amid takes place, a small quantity of white powder. This, on separation and examination under the microscope, presented the appearance of leucine, and when heated on platinum foil with nitric acid and then with caustic soda the yellow color and oily drop characteristic of this body were obtained. Leucine is not precipitated by mercuric nitrate and its presence no doubt has been due to some mercurous nitrate in the nitrate used. Spherules of leucine are apt to become incorporated in the crystals of glycocoll and may accompany it through several crystallizations, rendering nitrogen determinations, etc., inaccurate.

The evolution of hydrocyanic acid, on acidifying with hydrochloric acid after first heating with strong caustic potash, does not seem to be as satisfactory a reaction for glycocoll as at first appeared. In some instances I have obtained this reaction perfectly, and again on portions of the same sample it has failed. It seems to depend on the strength of the alkali and length of time of heating, and also on other conditions which I do not yet understand.

In the case of four samples of the sugar-cane amid I have distilled a known weight with a known excess of alkali, and received the distillate in successive portions of one cc. tenth-normal sulphuric acid, and measured each distillate. The actual figures obtained in one instance will best show what is to be learned from this.

0.2227 gram sugar-cane amid was distilled with 150 cc. water containing 0.3770 gram sodium hydroxide. The distillate was received into successive portions of one cc. tenth-normal sulphuric acid, the receiver being changed as soon as one cc. of acid was neutralized: litmus was used as indicator.

The volume of first distillate was 36.0 cc.

"	"	" second	"	"	18.2 "
"	"	" third	"	"	14.5 "
"	"	" fourth	"	"	14.3 "
"	"	" fifth	"	"	13.5 "
"	"	" sixth	"	"	12.3 "
"	"	" seventh	"	"	12.3 "
"	"	" eighth	"	"	12.3 "
"	"	" ninth	"	"	8.5 "

At this stage fifty cc. water containing 0.3770 gram sodium hydroxide were added and distillation continued.

The volume of tenth distillate was 7.5 cc.

"	"	" eleventh	"	"	16.4 "
"	"	" twelfth	"	"	30.4 "
"	"	" thirteenth	"	"	8.7 "

with only one-tenth cc. acid neutralized. As the distillation had been carried nearly to dryness and the evolution of ammonia very slight, the distillation was stopped. The total nitrogen set free as ammonia was 0.0169 gram, 7.58 per cent. or less than half that contained in the sample taken. This has been the general result obtained in other cases. The ammonia given off was small in amount until the alkali became concentrated, when the evolution was quite rapid, and approximately only half of the nitrogen was given off as ammonia, even when the distillation was carried nearly to dryness. The residue from the distillation with caustic soda was yellow in color, and, on being neutralized with hydrochloric acid, gave a jelly-like mass with brown flocks through it, and having the smell which is characteristic of the treatment of glue or fresh bones with alkali. This mass, when acidified with hydrochloric acid, gave off a small amount of hydrocyanic acid and resolved itself into a light brown solution with darker insoluble flocks floating through it. On filtering, neutralizing with ammonia, heating to boiling, and adding calcium chloride, a white precipitate was obtained presenting the characteristic microscopic appearance of calcium oxalate.

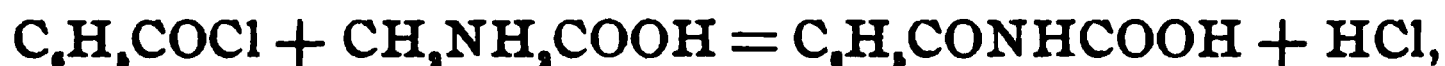
In view of the accepted formula for glycocoll,  $\text{CH}_2\text{NH}_2\text{COOH}$ , that is, a molecule containing only one atom of nitrogen, its behavior when heated with alkali is somewhat puzzling. We

must conclude either that the alkali attacks some molecules and not others, or different molecules in a different manner, or that the formula given above is not correct. It has been suggested that this formula should be doubled, giving a molecule containing two atoms of nitrogen, but a determination of the molecular weight by Raoult's method has not confirmed this. At any rate, whatever the formula and whatever the reactions when heated with alkali, it is clear from the number and character of the decomposition products, ammonia, hydrocyanic acid, oxalic acid, and the brown insoluble matter, that the reactions are by no means simple.

A much more satisfactory and conclusive test for the character of the sugar-cane amid I have found in the formation of hippuric acid from it and benzoic acid. The method of forming hippuric acid from these two bodies noticed in my first paper is one that requires heating to 160° C. in a sealed tube for ten or twelve hours. A much simpler and convenient method is by the action of benzoyl chloride on the amid. A watery solution of the amid is made slightly alkaline with caustic soda and benzoyl chloride added drop by drop, with constant shaking, until an excess has been added, and then made strongly alkaline with caustic soda. On cooling hydrochloric acid is added to strong acidity, when hippuric acid and the excess of benzoic acid are precipitated. These two acids are removed by filtration, separated by petroleum ether, and the hippuric acid crystallized from water. If the solution is dilute the hippuric acid will not be completely thrown down by hydrochloric acid for some hours, but if sufficient time be given the yield of hippuric acid is very nearly theoretical. If a mere qualitative test is wanted, hippuric acid can be obtained from the sugar-cane amid by this method in ten minutes. The hippuric acid so obtained has been identified by the microscopic appearance of the crystals; its sparing solubility in cold water, insolubility in petroleum ether, and solubility in acetic ether; also its behavior when heated and per cent. of nitrogen—seven and eight-tenths contained. I have obtained hippuric acid from horses' urine, and after purification it is not distinguishable by any test, physical or chemical, from that obtained from the sugar-cane amid.

The formation, then, of hippuric acid from the sugar-cane

amid is, I think, absolute proof that this amid is identical in constitution with glycocoll, *i. e.*, -amidoacetic acid. The ease with which the production of hippuric acid is brought about by the action of benzoyl chloride on the amid according to the equation



the purity of the hippuric acid obtained, and the ease with which it is separated, promise, I think, a simple and reliable method of estimating this amid in sugar-cane and its products.

LABORATORY OF KOHALA SUGAR CO.,  
KOHALA, HAWAII, H. I.

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### CORRESPONDENCE.

DECEMBER 27, 1897.

*To the Editor of the Journal of the American Chemical Society :*

DEAR SIR : The great success of the Second International Congress of Applied Chemistry leads to the belief that the next one, which is to be held in Vienna in July, 1898, will also be numerously attended. Nearly 2,000 members were present at the Paris meeting, and it required five large volumes to contain the report of its proceedings.

The undersigned have been appointed a committee in the United States, to promote the interests of the Third International Congress of Applied Chemistry, and beg leave to call the attention of the chemists of this country to that meeting, with the hope that many may be induced to attend. Those who subscribe and receive their membership cards will be entitled to all reductions in rates going to and coming from Vienna, which are arranged for members of the Congress. During the Paris meeting, the French line of steamers reduced its rates thirty-three per cent. to members of the Congress. It is hoped that an arrangement can be made with some of the steamship lines during the coming summer for a similar reduction, although the committee has not yet been informed of any arrangement of this kind.

The opportunity of meeting distinguished chemists from all parts of the world should not be lost sight of, and will doubtless be appreciated by the American members. The scientific work of the Congress will be divided into the following sections :

Section 1. General analytical chemistry and apparatus, Dr. George Vortmann, Wien, IV Schanmburgergasse 16, chairman.

Section 2. Food, medicinal and pharmaceutical chemistry, Dr. Ernst Ludwig, Wien, XIX Bilothestrasse 72, chairman.

Section 3. Agricultural chemistry, Prof. E. Meissl, Wien, II Trummerstrasse 3, chairman.

Section 4. Chemistry of the sugar industry, Prof. Friedrich Strohmer, Wien, IV/2 Schönburgstrasse 6, chairman.

Section 5. Chemistry of the fermenting industries, Prof. F. Schwackhäfer, Wien, XIX Karl Ludwigstrasse 74, chairman.

Section 6. Chemistry of wine-making, Dr. L. Rosler, Wien, Physiologische Versuchsstation, chairman.

Section 7. Inorganic chemical industries (manufacture of sulphuric acid, soda, etc.), Herr Paul Seybel, Wien, III, Reissnerstrasse 50, chairman.

Section 8. Metallurgy and explosives, Prof. Franz Kupelwieser, Wien, I Franzenring, chairman.

Section 9. Organic chemical industries, Dr. Hugo Ritter von Perger, Wien, IV Gusshausstrasse 23, chairman.

Section 10. Chemistry of the graphic industries (photo-chemistry, photography, etc.), Dr. Josef Maria Eder, Wien, VII West Cohnstrasse 25, chairman.

Section 11. Didactic chemistry, Prof. Franz Lafar, Wien, Technische Hochschule, chairman.

Section 12. Electrochemistry, Dr. Karl Kellner, Hallein, Salzburg, chairman.

All persons desiring to become members and wishing further information on the subject of the Congress can secure copies of the provisional reglement by addressing the chairman of the committee, Washington, D. C.

Excursions, visits to localities of interest, banquets, etc., will be arranged for and definitely announced at a later period. Papers in German, French, and English will be accepted, and authors are requested to communicate with the several chairmen and send them titles of papers and subjects which they would like to have discussed.

All persons intending to become members of the Congress may receive a membership card from the secretary, Dr. F. Strohmer, by sending twenty-one francs to his address, IV/2 Schönburg-



strasse, Nr. 6, Vienna, Austria. If preferred, members may send \$4.30 to the chairman of the American committee, who will transmit the proper amount to Dr. Strohmer.

The provisional officers of the Congress are as follows :

President of Honor—Hofrath Prof. Dr. Alexander Bauer.

Active President—Regierungsrath Dr. Hugo Ritter v. Perger. Professor in the Royal Imperial Technical High School of Vienna.

Vice-President—Regierungsrath Dr. Josef Maria Eder, Director of the Royal Imperial Graphic School in Vienna.

Secretary—Prof. Dr. F. Strohmer, Director of the Experiment Station for Beet-Sugar Industry, Vienna.

Respectfully,

H. W. WILEY, Dept. of Agriculture, Washington, D. C., Chairman.

W. O. ATWATER, Wesleyan University, Middletown, Conn.

PETER T. AUSTEN, 11 Broadway, New York.

C. F. CHANDLER, Columbia University, New York, N. Y.

B. F. DAVENPORT, 161 Tremont St., Boston, Mass.

C. A. DOREMUS, 17 Lexington Ave., New York, N. Y.

C. B. DUDLEY, Altoona, Pa.

W. L. DUDLEY, Vanderbilt University, Nashville, Tenn.

WM. P. MASON, Rensselaer Polytechnic Inst., Troy, N. Y.

WM. MCMURTRIE, 100 William St., New York, N. Y.

C. E. MUNROE, Columbian Univ., Washington, D. C.

A. A. NOYES, Mass. Inst. Technology, Boston, Mass.

T. B. OSBORNE, Agr. Expt. Station, New Haven, Conn.

IRA REMSEN, Johns Hopkins Univ., Baltimore, Md.

W. B. RISING, University of California, Berkeley, Cal.

EDGAR F. SMITH, Univ. of Pa., Philadelphia, Pa.

F. G. WIECHMANN, 771 West End Ave., New York, N. Y.

FRANCIS WYATT, 39 South William St., New York, N. Y.

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### OBITUARY.<sup>1</sup>

CHARLES EDWARDS COLBY was born in Lawrence, Mass., October 18, 1855. He was a direct descendant of Anthony Colby, who came to this country from Beccles, England, with Governor Winthrop's company, in 1630; and was also closely related to Captain Valentine Bagley, the subject of Whittier's celebrated poem entitled "The Captain's Well."

He early manifested an interest in electricity and chemistry, making a successful arc lamp, when only fourteen years old,

<sup>1</sup> Read at the meeting of the New York Section, December 10, 1897.

from the movement of an old clock; and constructing magic lanterns, spectroscopes, and other physical apparatus, from the crudest of materials. In 1868 he came to New York City, and entered Grammar School No. 35, in West 13th St., then under the charge of Dr. Hunter, from which he graduated in 1872, and soon after went to Germany to study, returning in time to take the entrance examinations for Columbia College in 1874. His energy and ambition are well shown by his attempt to carry on three courses at once—civil engineering, mining engineering, and chemistry,—a privilege then allowed by the college, and which would undoubtedly have been successful but for an attack of pneumonia in 1876, which compelled him to relinquish for a time his chemical studies, but permitted the completion of the two other courses, and, on graduation in 1877, he was awarded the degrees of C.E. and M.E.

He then accepted the position of Private Assistant to Professor Chas. F. Chandler, and was engaged for several years, under Dr. Chandler's direction, in many important investigations, especially in the field of organic chemistry. Among these investigations should be mentioned that of artificial alizarine, in connection with several suits brought into this country under the Graebe and Liebermann patent by the representatives of the Badische Anilin und Soda Fabrik, and which involved, first, the question of the identity of the artificial with the natural alizarine, and, later, the relations of flavopurpurine and anthrapurpurine to the original patent. There were also investigations upon the sulphanilic acid colors, naphthionic acid colors, thionin colors, the various sulpho acids of rosanilin, naphthol yellow, the composition of the archil imported into this country, the manufacture of chloroform from acetone, and many other similar subjects.

The ability exhibited in these researches led to his appointment, on October 6, 1884, as a fellow in chemistry, and the separate instruction in organic chemistry was thereafter confided to him. On June 7, 1886, he was advanced to the grade of instructor in organic chemistry; and on March 3, 1890, the chair of adjunct professor in organic chemistry was created for him, and this position he held at the time of his decease on October 15, 1897.

During these thirteen years of teaching and investigation, he has added very materially to our store of knowledge in his chosen sphere of activity, and many important researches have been carried on in the laboratory of organic chemistry either by him personally, or under his immediate supervision. The production of the aromatic sulfoxides by the action of thionyl chloride and aluminum chloride upon the hydrocarbons of the benzene series; the preparation of aromatic nitriles from aromatic acids and fatty nitriles; the preparation of the imids of bibasic fatty acids by the interaction of the nitrile and the acid; the production of the corresponding imids of the bibasic aromatic acids by heating together the acid and a fatty nitrile; these, and many other organic researches, might be recalled in this connection.

Professor Colby was a man of most versatile attainments, being not only a chemist of exceptional ability, but also an expert in physics, mathematics, mechanical drawing, and music. As a teacher, he was most careful and painstaking, devoting his entire time to his students, and assisting and encouraging them by every means in his power. His lectures were models of concise classification, and his explanations were always lucid and full. A deep and analytical thinker, thoroughly imbued with the spirit of the true scientist, which forgets all else in the search for truth, he inspired his students with much of his own enthusiasm, and finally sacrificed his life in the pursuit of the science he loved so well.

It was most unfortunate that his physical equipment was not at all in keeping with the urgings of his ambition, and for the last few years of his life his constantly increasing weakness, brought on largely by overwork, practically debarred him from all laboratory investigation. In spite of his illness and the distressing realization of the inability of the body longer to respond to the calls of the energetic and brilliant mind, he bore his sufferings with the most heroic and uncomplaining fortitude, and fought the battle bravely to the end.

Columbia University, and the world of science, have suffered a very grievous loss in the death of this able and devoted scientist.

MARSTON TAYLOR BOGERT.

## NEW BOOKS.

**ELEMENTS OF ELECTROCHEMISTRY.** BY R. LÖPKER. Translated by M. M. PATTISON MUIR. Philadelphia: J. B. Lippincott Co. 1897. vii + 223 pp. Price, \$2.50.

We have used the German edition of this text-book in our class in electrochemistry and can heartily recommend it as the only book at all suitable for such purposes, and now the English translation has made it still more useful. Still, excellent though the book is, we cannot help wishing that Mr. Muir had written a new book, giving particular attention to the incomparable experiments of Faraday on Electrochemistry, instead of making this translation.

The book is somewhat overbalanced. The osmotic theory, as illustrated by osmotic pressure, boiling-point, and freezing-point, occupy nearly forty pages. We found it far better to substitute a couple of lectures for this part. For the student of electrochemistry the lectures were sufficient.

The book opens with the Phenomena of Electrolysis. A number of simple and instructive experiments are described, but we regret to note the absence of Faraday's simple but elegant qualitative experiments on this subject. Then follow chapters on Hittorf's Transport-Numbers, The Law of Kohlrausch, The Dissociation Theory of Arrhenius, Osmotic Pressure, Vapor Pressure of Solutions, Boiling-Points and Freezing-Points of Solutions, Summary, Aqueous Solutions of Electrolytes, Liquid Cells, Daniell Cells, Reduction and Oxidation Cells, The Solution Pressures of the Metals, Intensity of Fixation and Polarization, Irreversible Cells, Accumulators, and The Energetics of Galvanic Elements. Nearly all the subjects are illustrated by good and simple experiments, most of them of such a nature that the student can construct the necessary apparatus himself.

C. L. SPEYERS.

**MANUAL OF QUALITATIVE CHEMICAL ANALYSIS.** BY THE LATE DR. C. REMIGIUS PRESENUS. Authorized Translation by HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. New edition, thoroughly revised from the Sixteenth German Edition. New York: John Wiley & Sons. 1897. xvii + 748 pp. Price, \$5.00.

In the present translation Prof. Wells has given to American

and English students an admirable reproduction of the last German edition of Fresenius' work, which appeared in 1895. The plan laid down in the earlier German editions has been closely followed in all the later issues, and in the present version the changes consist mainly in additions to parts dealing with methods of detection and separation, and in the elaboration of details. These changes are, however, of such a character as to give a new aspect to the work.

Few innovations are noticed in the chapters upon preparation and testing of reagents.

The reactions of the common bases and acids are treated after the manner of the older editions, yet this part of the work has received important additions, and in the case of reactions already well known, the methods for their production are described with such increased attention to the details of experiment as to insure greater accuracy of analytical results. Corrections are made in formulas which have been long in use, while in other cases (*e. g.*, the basic carbonates) definite formulas have been often purposely omitted. Many newer methods are cited for the separation of the metals of the various groups, and the student is given a greater scope for the exercise of judgment in selecting a method adapted to a special case. The reactions of the rarer metals and their separation are discussed in a manner which reflects very satisfactorily the recent literature of the subject.

In the Systematic Course of Analysis important improvements are made in the details of methods which have long been favorably known.

The chapter upon the Analysis of Simple Compounds (which was dropped in the last English translation) has been retained, although its value may be somewhat questioned.

Qualitative analysis applied to water possesses less value than formerly, in view of recent advances in methods of water examination. Nevertheless the process given for the purpose is very complete.

Under Toxic Analysis the methods described for the detection of arsenic and other poisonous metals are mainly those of the last edition. They are supplemented by an excellent discussion of the purification of the reagents needed for such work.

Important improvements occur as regards methods for the detection of phosphorus and of other non-metallic poisons.

Abundant literature references give increased value to the entire work. The older system of equivalent weights, retained by Fresenius even in the latest German edition, has been wisely suppressed as serving no good purpose.

The student of Prof. Wells' book cannot fail to be impressed by its accuracy of statement and the painstaking care with which the directions given him are formulated.

The work of the translator has been performed in a thorough manner, and it may be said that the new English version will be welcomed by chemists everywhere. F. C. PHILLIPS.

**THE PHARMACIST AT WORK.** BY WILLIAM C. ALPERS. Philadelphia: J. B. Lippincott Co. 1898. ix + 326. Price, \$1.50.

The usual review methods of scientific works are hardly applicable to this book. The story, in its outward features at least, is a story of the past and appeals with especial force to men who look backward in pharmacy. The preceptor and apprentice are before us again; throughout twenty-four chapters and 326 pages, we are captivated by a pithy dialogue wherein the author not only treats of pharmaceutical manipulation and the chemical and physical principles underlying them, but also comments on many possibilities with which a pharmacist's life is confronted, portraying with much refinement not a few of the frailties of human nature. From beginning to end, every page bears testimony to the author's love for his art and the earnestness of the moral and ethical principles he advocates.

Mr. Alpers, a typical German pharmacist, who came to America just after the Franco-German war, and who has thorough command of his subject, takes the opportunity to make some timely suggestions to modern druggists. He points out (p. 41) the great unknown in alkaloidal and Galenical chemistry as applied to pharmacy, and it is to be hoped that his earnest words will arouse many pharmacists who have the time but waste it by indifference to scientific thought. He informs the reader (p. 56) that tinctures are superior to tablets as medicine carriers, but he realizes also that tablets are so easily counted into a box without involving the "bother" of laboratory work, as to render it possible that better preparations will suffer.

While considering plasters, pills, emulsions, decoctions, syrups, and other classes of preparations, the author instructs and interests not only the clerks whom he addresses, but any pharmacist who reads after him and wishes to refresh his mind or to learn anew. Scarcely a subject of value in drug-store manipulation but is well treated, and the errors detected in the book are trivial or typographical, such as the word carbonate (p. 197) instead of carbamate. The reviewer picked up the book in the expectation of a task in the "twice told tale;" he read it through with unalloyed interest, forgetting the task. It is a book for pharmacists to read, to think over, to read again; it is a book for the young druggist without an instructor, as well as to refresh the mind of the teaching pharmacist who is an instructor professionally. Especially should it be read by those who are contented with the belief that the art of pharmacy has no higher standard than the counting out of factory-made pills and tablets.

JOHN URI LLOYD.

A DICTIONARY OF CHEMICAL SOLUBILITIES, INORGANIC. BY A. M. COMEY. New York: The Macmillan Co. 1896. xx + 515 pp. Price, \$5.00.

This new Dictionary of Solubilities is limited to substances not containing carbon, exception being made in the case of the carbonates, cyanides, carbon monoxide and disulphide, and a few others. While a complete compilation of data for all carbon compounds would have delayed its appearance, it is to be regretted that the author did not include some of these which are of importance to inorganic chemists. A few pages devoted to the oxalates, acetates, citrates, tartrates, the commoner alcohols and a few other organic compounds, would have added much to the value of the work without materially increasing its size; we are at a loss to understand why carbonyl chloride, nickel carbonyl, or an aromatic derivative like potassium carbonyl should be preferred to these. The plan of placing oxy- and sulpho-salts under the acid and other metallic compounds under the metal, has the precedent of use by some dictionaries of chemistry, but we think that classification under the negative radical in all possible cases would have been better as more consistent and as facilitating reference and comparison. There is

no very good reason for classifying simple negative radicals in one way, and compound in another.

The list of compounds seems to be tolerably complete; we note, however, that paracyanogen and the dicarbide and oxycarbides of silicon are omitted, while cyanogen and carborundum are to be found. Minerals are properly included, but unfortunately often without data. The plan adopted of giving "chemical" as well as "physical" solubilities, is obviously the only one suitable from a practical standpoint.

The author attempts in his preface to justify his course in giving all available data without distinction as to reliability and without eliminating actual contradictions, on the ground that it would be impossible to test all the statements experimentally. This is quite true, but we cannot regard it as a sufficient excuse for the many superfluous and contradictory statements which have been admitted. One who writes a text- or handbook must use some discrimination if he would avoid appearing not only as a very poor chemist, but as a hack of the worst sort. We are told, for instance (p. 178), that free hydroxylamine is known only in solution, while just below de Bruyn is quoted, according to whom it is a crystalline solid. It is absurd to waste space on vague statements as to solubility (see  $H_2$ ,  $HNO_3$ ,  $H_2SO_4$ , and hundreds of others), when these are to be followed by numerical data. The space and cost of printing such superfluities might well have been devoted to giving solubility curves of the best-studied substances. On the contrary, important data are often omitted. Much is known of the solubility of water in, and its miscibility with, other liquids, yet the author's data comprise but four lines, together with some vague generalities on its being the most universal solvent (p. 499). The works of Fleitmann, Maddrell, and others, on metaphosphates are fully abstracted, but no mention is made of the later, and in part revolutionary work of Tammann. Nothing is said of the existence of two forms of magnesium pyrophosphate, differing in their behavior towards acetic acid, a fact of analytical importance. Many erroneous or ambiguous statements are to be found, which can only be attributed to carelessness. Thus, on pp. 148, 237, the didymium metals are written *neodidymium* and *praseodidymium*; hydroxylamine hydrochlorate is written hydroxylamine *chloride*.



(p. 178) ; we are told (p. 316) that phosphorus is decomposed *by* water, *by* nitric acid and *by* alkalies, and similar statements are made concerning strontium (p. 385), and mercury (p. 225) ; phosphorus is said to be "easily soluble in  $\text{PCl}_3$ ," which is not a case of "solid solution," but the author's way of stating the reaction between these bodies. "Filtered rain water was found to contain 20 mg. Zn per l." (p. 501), instead of *to dissolve*. On p. 471 both the properties and formulas of the thionyl and sulphuryl chlorides and amides are hopelessly confused.  $\text{P}_2\text{O}_5$  is said to dissolve in water, forming  $\text{H}_3\text{PO}_4$  (p. 318), instead of  $\text{HPO}_3$ .

These faults, however, which can be found by scores, are far more pardonable from the practical standpoint than the author's system of references. In a work of this kind the full reference for *every* statement which is not a commonplace, should be given, and repetition avoided by the use of foot-notes. No foot-notes are used here, and a large percentage of the data are given without quoting any authority or reference whatever. On nearly every page one finds the name of the authority given without reference to the original sources, even when no repetition would have been incurred and where the original must have been easily accessible, although the author says he has always consulted the original memoirs when possible. This omission is absolutely unjustifiable, though unfortunately not without precedent. In many cases data from different sources are grouped in one paragraph with a single reference at the end, in such a way as to make this appear to cover the whole ; thus, on page 317, Schiff is credited with all the solubility data of phosphorus pentachloride, while in reality only the last mentioned is due to him.

A dictionary of solubilities which one can consult with full confidence that he is getting the best information available, and which he can use as a guide to the original sources, is greatly needed, and it is to be regretted that the author has not taken more care with respect to the points above noted. Nevertheless, imperfect as it is, the work is extremely valuable, and in most cases will answer the practical requirements. The author has evidently devoted an enormous amount of labor to its preparation, and he deserves the thanks of all working chemists.

H. N. STOKES.

**THE PRINCIPLES OF CHEMISTRY.** BY D. MENDELÉEFF. Second English edition, translated from the sixth Russian edition by G. KAMENSKY, edited by T. A. LAWSON. 2 vols. pp. xviii + 621 and 518. New York: Longmans, Green & Co. 1897. Price \$10.00.

Since its discovery by Mendeléeff, the Periodic System has been made the basis of several treatises on chemistry. A book in which it is rigidly adhered to, like Ramsay's "System of Inorganic Chemistry," may be valuable to the advanced student for reference and comparison, but would be but poorly suited to teaching chemistry to beginners, even of mature age. Some familiarity with a few of the typical elements and their compounds, and with the more important laws, is necessary, before the student is in the position to grasp the idea of periodicity. Mendeléeff does not carry his favorite idea too far; his book affords an admirable illustration of the proper method of adapting the Periodic System to the requirements of beginners, and it is difficult to conceive how it could be improved in this respect. The writer of this review has had the opportunity of learning by practical experience how admirably his method works in the classroom, and can heartily recommend the work as a model both to writers of text-books and to those who are arranging courses of lectures in general chemistry.

After an introductory chapter treating of combination, decomposition, reactions, elements and compounds, and other preliminary matter, the reader takes up the study of water, its properties, composition, and compounds. This leads to the consideration of hydrogen and oxygen, acids, bases, and salts, which are followed by nitrogen, the air and the compounds of hydrogen, oxygen, and nitrogen. This has the advantage not only of introducing typical elements at the start, but also of calling the beginner's attention to some of the substances most familiar in every-day life, which are much more likely to interest him than unheard-of objects. Not until the 299th page does the author begin the consideration of the atomic theory and Avogadro's hypothesis, from which it will be seen that it is his custom to state first the facts, then the generalizations, and last of all the hypotheses based on these—a most admirable course, which it is to be wished all writers of text-books would follow. Carbon compounds are considered next, after which follows a chapter on

sodium chloride, hydrochloric acid, and the law of mass action, the importance of which is much more strongly emphasized than is usual. Chapters on halogens, the alkali and alkaline earth metals and on valency and specific heat bring the first volume to a close, leaving the student in a position to understand the Periodic Law, which takes up the first chapter of the second volume. The remaining elements, which are treated in a strictly systematic way, take up the remainder of the volume. The work is supplemented by three appendices, consisting of two lectures delivered in London on "An Attempt to Apply to Chemistry One of the Principles of Newton's Natural Philosophy," and on "The Periodic System," and an essay on "Argon, a New Constituent of the Atmosphere," which are good illustrations of the style and speculative tendencies of the author. Argon was discovered after the revision was practically finished, and therefore appears only in foot-notes and in the appendix, while helium was found too late to be taken note of.

The book is therefore not a treatise on theoretical chemistry, but a descriptive work in which an unusual degree of attention is given to the principles of the science. The author has endeavored to adapt it to both beginners and advanced students, and has therefore placed the most important material in the text, supplementing this with numerous foot-notes, which constitute at least one-half of the book, and which contain more detailed information as well as numerous digressions. He recommends beginners to omit the foot-notes on the first reading.

The treatment throughout is highly original, and in few works of the kind are the personal views of the author so apparent on every page. This renders the book peculiarly attractive and suggestive to the mature chemist, but it may be questioned whether it is desirable for the younger student to find important subjects treated in as one-sided a way as is sometimes the case—for example, in a book on the Principles of Chemistry one would look for some statement of current ideas of molecular structure, yet this is not to be found. The author uses no structural formulas and does not even explain what they are—at most, he admits that they may have some application to carbon compounds, but does not hesitate to say that the day of structural chemistry (in its present sense) is past (vol. 2, p. 466). He

frequently compares molecules to planetary systems. His inclination to speculate and generalize is everywhere evident, and while it often leads to valuable and suggestive results, it is occasionally carried to an extreme, as when we are told that "gases which are easily liquefied (by pressure and cold) are more soluble than those which are liquefied with difficulty," or when he states his opinion that there is a possible mysterious connection between the *eight* groups of the Periodic System, the *eight* major planets, and the *eight* satellites of Saturn (vol. 2, p. 463), a view which may be pardoned in the mind which perceived the Periodic Law, but which would certainly be ridiculed in any lesser.

A physical chemist of the new school would probably find fault with the treatment of the subject of solutions. As is well known, Mendeléeff is an adherent of the "hydrate theory." It is one of his favorite subjects and he alludes to it on every possible occasion. He defines a solution as an "homogeneous liquid system of unstable dissociating compounds of the solvent with the substance dissolved" (vol. 1, p. xiii) and elsewhere in similar terms (vol. 1, pp. 106, 111, etc.). Cryohydrates are regarded as definite compounds and nothing is said of eutexy. The theory of electrolytic dissociation in solution is barely alluded to and then only to condemn it (vol. 1, pp. 92, 108), while its real nature is not set forth. The new edition mentions the more important investigations on the influence of dissolved substances on the freezing-point and boiling-point, but without any serious effort to explain the different behavior of electrolytes and non-electrolytes. For these reasons the student should consult at the same time some work in which the newer views are more fully stated. In general, the new edition takes sufficient account of recent investigations, but in a few instances these have been overlooked, as in the case of the atomic weight of oxygen (given as 15.96), and the sulphur and nitrogen compounds of phosphorus. The translation is generally clear and idiomatic, and the book is practically free from typographical errors, except that names of persons are frequently misspelled (Staas for Stas, Ebelmann for Ebelman, Schönebein for Schönbein, Clark for Clarke, etc.). The index contains many errors of omission and commission.

We conclude with a quotation from the author's preface: "Knowing how contented, free, and joyful is life in the realm of science, one fervently wishes that many would enter its portals. On this account many pages of this treatise are unwittingly stamped with the earnest desire that the habits of chemical contemplation which I have endeavored to instil into the minds of my readers will incite them to the further study of science. Science will then flourish in them and by them, on a fuller acquaintance not only with that little which is enclosed within the narrow limits of my work, but with the further learning which they must imbibe in order to make themselves masters of our science and partakers in its further advancement."

H. N. STOKES.

**INCOMPATIBILITIES IN PRESCRIPTIONS, FOR STUDENTS IN PHARMACY AND MEDICINE, AND PRACTICING PHARMACISTS AND PHYSICIANS. BY EDSEL A. RUDDIMAN, PH.D., M.D. 1897. New York: John Wiley & Sons. v + 264 pp. 8vo. Price \$2.00.**

This is a book for the pharmacist, rather than a book for chemists, as the author states in his title-page. It is divided into two parts:

Part I details the principal reactions and physical properties of the medicinal substances most used in compounding prescriptions. It deals chiefly with solubilities and precipitants, changes of color, and behavior when mixed dry or rubbed up in a mortar. This part of the book is essentially a compilation from drug journals, and pharmaceutical and chemical works. The author has, however, confirmed many of the statements. The compilation has involved a large amount of work, and references have been given, in most cases, to the sources of information. The author does not tell us how many of these statements he has confirmed, but in some cases he records his own results, when they contradict the statement he quotes, leaving us to infer that he has found the rest of the statements correct as quoted. The substances are taken up alphabetically, and only the Latin names are used, which might with propriety have been followed by the chemical name. Another very important omission, which greatly lessens the value of the book, is that it does not give the degree of solubility of the substance in water, alcohol, or diluted alcohol. These facts are especially of service to the pre-

scriber. This omission, it seems to us, is the most serious defect in this part of the book, if we assume that the statements have all been confirmed. Without such confirmation, it would hardly be safe to trust to the accuracy of statements taken from the current journals.

The author has quoted freely from Watts' Dictionary as revised by Muir and Morley, Allen's Commercial Organic Analysis, and other standard authorities.

Part II consists of a list of 325 complete prescriptions, written so as to include almost the whole range of the substances mentioned in Part I, in different combinations, with critical and explanatory notes upon each one. This part of the book, we believe, is almost entirely original, and bears evidence of great care, and many of the comments are based upon a trial of the prescriptions in hand. These prescriptions and notes are supplemented by an excellent reference index, by means of which it is possible to refer to prescriptions containing any of the drugs mentioned, as well as to the nature of the other ingredients of the mixture. A useful table is appended, giving the effect of rubbing together equal weights of thirty-one solid organic substances, including most of the recently introduced synthetic compounds. As a whole, the book bears evidence of careful selection, conciseness, practical knowledge of the needs of the pharmacist, and systematic arrangement of facts.

In spite of the defect above noticed, we believe that this book is a valuable contribution to pharmaceutical literature, and a very useful one as well. If every young physician should study it carefully, those who have to swallow his mixtures would be much better treated than at present. Every pharmacist should have it at his prescription case and consult it freely.

E. H. BARTLEY.

THE EARLY HISTORY OF CHLORINE. PAPERS BY CARL WILHELM SCHEELÉ(1774), C. L. BERTHOLLET(1785), GUYTON DE MORVEAU(1787), J. L. GAY-LUSSAC and L. J. THÉNARD (1809). ALEMBIC CLUB REPRINT NO. 13. Edinburgh: W. F. Clay. 48 pp. 12 mo. Cloth. Price 1s. 6d.

The Alembic Club of Edinburgh is doing students of physical science real service in reproducing in inexpensive form the researches of early masters in chemistry. This volume should

have preceded the earlier one (No. 9) on "The Elementary Nature of Chlorine," by Humphry Davy, the original of which bears the date 1810.

The first paper, by Scheele, "On Manganese and its Properties," is translated from the Transactions of the Royal Academy of Sciences of Stockholm, and shows his clear and remarkably correct views as to the nature of the substance accidentally obtained when treating black oxide of manganese with hydrochloric acid. Scheele writes concisely, using the language of the phlogistic theory, which forms a great contrast to that used by Berthollet in the second paper; Scheele's essay bristles with Latin terms, such as *acidum salis*, *spiritus salis ammoniaci*, and *alkali fixum*; Berthollet's essay shows the admirable influence on the language of chemistry exerted by the contemporaries of Lavoisier, and reads much more like a modern treatise.

A short extract from a Memoir on Nomenclature by de Morveau, is interesting since it introduces the word *radical*, not *radicle*, as some chemists would have it.

The Memoirs by Gay-Lussac and Thénard exhibit the share these chemical philosophers have in the investigation of "dephlogisticated marine acid," prior to the time of Davy. Davy, it must be remembered, demonstrated that the new gas contained no oxygen, and that it was of an elementary character; to him also is due the name chlorine.

H. CARRINGTON BOLTON.

AN OUTLINE OF THE THEORY OF SOLUTION AND ITS RESULTS. BY J. LIVINGSTON R. MORGAN, PH.D. Small 8vo. New York: John Wiley & Sons. 63 pp. Price \$1.00.

The period of unrest and debate in the modern theory of solution is, in the main, at an end. This theory has substituted for vague representations of isolated facts, clear and concise conceptions based on plausible hypotheses and stated with mathematical precision. Osmotic pressure, diffusion, lowering of freezing-point, and raising of boiling-point, etc.,—all these properties of solutions have been accounted for and brought into causal relationships, and "the hundred-year problem of the voltaic cell" has finally been solved.

A period of quiet but intense activity has now set in. Workers attracted by the brilliancy of the results thus far obtained,



are busy in clearing up obscure points and extending the field of inquiry.

Now, that this theory has been generally adopted by those whose work puts them in more immediate touch with it, a desire springs up in those whose interests are in more remote connection thereto to get some knowledge of its import and aspect. The author has responded in a most creditable manner to this demand. He gives in clear language the gist of the theory of solution, how it has arisen, and what it is to-day. The treatment and style is as non-mathematical as the nature of the subject permits, but it must be borne in mind that a criterion of the degree of advancement of a branch of science is the possibility of clothing its results in mathematical dress, and he who would keep up with the times must needs acquire at least the elements of higher analysis.

The chapter on analytical chemistry from the standpoint of electrolytic dissociation should be read and digested by every teacher and student of analytical chemistry as well as by every professional analyst; it is law and order introduced into empiricism.

Such a *résumé* is invaluable; it presents in compact and inviting form facts of great importance having a more or less direct bearing upon every branch of chemistry. Its perusal will show that the work of the physical chemists is not so abstruse and barren of practical results as it is too often supposed to be. The book cannot be too strongly recommended.

C. E. LINEBARGER.

THE PRINCIPLES OF MATHEMATICAL CHEMISTRY. THE ENERGETICS OF CHEMICAL PHENOMENA. BY DR. GEORG HELM. Authorized translation from the German by J. LIVINGSTON R. MORGAN, PH.D. Small 8vo. vi + 228 pp. New York: John Wiley & Sons. Price, \$1.50.

The impression the reviewer got from reading the original German of this work was that, while the subject-matter was excellent, the treatment was faulty, and he now feels that it is a pity that the translator did not edit rather than merely translate the book. While the author's purpose was "to collect the results, according to the deductive method, of the investigations in the realm of general chemistry," the translator's "desire to spread the knowledge of physical chemistry" would have un-



doubtedly been better fulfilled if more power of editorship had been exercised. The translation, however, has been done very well. One seldom comes across passages where he must think in German while reading English. On the whole, the translation may be reckoned an improvement on the original, especially in mechanical execution.

The book is an application of energetics to the problems of chemistry. The division of energy into intensity and capacity factors is maintained, and generally Ostwald's ideas on energy have been accepted. The book is divided into four parts, treating of energy, entropy, chemical intensity, and degrees of freedom of chemical phenomena, respectively. Naturally, thermodynamics enters largely into the treatment of the first two parts. Of most interest to chemists, however, is the part treating of chemical intensity or affinity. In it we find an application of Gibbs' "Equation Twelve" to the phenomena of osmotic pressure, diffusion, and other topics upon which the modern theory of solution has thrown so much light. Also, Gibbs' "Phase Rule," that competent guide through the labyrinth of chemical equilibria, is well, although briefly, taken up by the author.

In certain points the translation is open to criticism. Thus, the numbers of reacting molecules in a system of reacting numbers (called by the translator "exchange numbers" probably as a close translation of *Umsatzzahlen*) which the author, following the initiative of Planck, denotes by the Greek letters  $\nu_1, \nu_2, \nu_3, \dots$ , the translator writes  $\nu_1, \nu_2, \nu_3, \dots$ , throughout; this is to be regretted as tending to cause confusion, inasmuch as  $\nu$  generally designates volume.

Also, the translation reads (p. 74) "third principle of thermodynamics" where *thermochemistry* is meant.

Furthermore, a word might be said in regard to the use of the words *speed* and *velocity*. While they both express the time-rate of change of position, velocity has the additional notion of direction; velocity is directed speed. A chemical reaction considered with reference to time is not a directed quantity or *vector*; consequently, we should speak of the speed and not the velocity of a chemical reaction.

While the book does not require very much mathematical

knowledge on the part of the reader, it presupposes that he has a not inconsiderable acquaintance with the facts and laws of physical chemistry. To those up in this particular the book will be of service from its unity of arrangement and broadness of treatment.

C. E. LINEBARGER.

**ELECTRIC SMELTING AND REFINING, BEING THE SECOND EDITION OF ELECTRO-METALLURGIE.** BY DR. W. BORCHERS, translated, with additions, by WALTER G. McMILLAN. London: Charles Griffin & Co., Ltd.; Philadelphia: J. B. Lippincott Co. 1897. xx + 416 pp. Price \$6.50.

This book treats of the extraction and refining of metals by the electric current and includes the electrolysis of aqueous solutions as well as electric smelting proper, but not electrolytic analysis, electroplating, or electrotyping. The introduction describes concisely the modern theory of migration of ions, with references to larger works, the translator adding some wise remarks upon the cost of electrometallurgical works. Additions by the translator supplement and broaden the work of the author throughout the book.

The following metals are treated: Magnesium, lithium, beryllium, sodium, potassium, calcium, strontium, barium, aluminum, cerium, lanthanum, didymium, copper, silver, gold, zinc, cadmium, mercury, tin, lead, bismuth, antimony, chromium, molybdenum, tungsten, uranium, manganese, iron, nickel, cobalt, and the platinum group. In considering each metal there is a good description of the properties of the metal, its natural occurrence, and, for comparison, a brief description of the ordinary methods of its extraction. Then follows a description of the attempts to use the current in the production and manipulation of the metal.

In general this history is remarkably full and complete, but with a few notable exceptions. Much purely experimental work is described, together with many impracticable propositions. The record of these, however, is valuable, particularly for shaping future investigations. The author quotes freely from original sources, with abundant references, and discusses the important propositions. He adds many valuable points from his own extensive and ingenious experience. He forgets, however, like a vast majority of people, that a patent is a crea-

ture of law and discusses patents without due regard to the patent laws of various countries. He often treats a patent too seriously.

A chapter is devoted to the carbides of the alkaline earth metals, but no mention is made of carbide of silicon, carborundum.

The author considers it impracticable to extract the common metals directly from their ores, by the current. They must first be smelted by ordinary means to crude metal to be refined by the current or else they must be leached and the solutions electrolyzed, with regeneration of the solutions for reuse, or utilizing the anode reactions for producing useful products.

While promising processes are being developed the commercial condition of the art is briefly this: No metal, with the possible exception of sodium in alloys and magnesium, is produced directly from native ores by the current. Only two important metals, sodium and aluminum, are produced by electric smelting proper. Silver, and incidentally gold, and vast quantities of crude copper are electrolytically refined. A few processes are applicable under special conditions.

Although this book is essentially German in its conception and execution, it must prove of great value to workers in the field. It is profusely illustrated, has a full table of contents and a good index.

FREDERIC P. DEWEY.

THE BOOK OF THE DAIRY. TRANSLATED BY C. M. AIKMAN AND R. P. WRIGHT from the German work of W. FLEISCHMANN. London and New York: D. Van Nostrand Co. xxiv + 344 pp. Price \$4.00.

This work is a translation of the first edition of Dr. Fleischmann's "Lehrbuch der Milchwirtschaft." Since the translators have completed their work, a second and improved German edition has been published. The translated edition does not include the important dairy work of the last six or seven years. This seriously impairs the usefulness of the book; as an example, the probabilities regarding the variations in the size of the fat globule are considered, while no reference is made to the recent work relating to this topic. Some of the old methods for testing milk as Marchand's butyrometer should have been replaced by more reliable and modern ones as Babcock's or Gerber's centrifugal method; then there would have been no necessity to have said, "It is to be hoped that a reliable method of deter-

mining fat will soon be discovered, so convenient and at the same time so cheap that it may be capable of being employed on small farms."

The strongest features of the work are: The part relating to the testing of the efficiency of separators; and the chapter on cheese-making. The figures for the creaming efficiency of separators are old and misleading, on account of the great improvements which have been made in their manufacture. The methods which are employed for testing their efficiency are however scientific. It is refreshing to read that when separator skimmed milk contains much less than one-tenth per cent. fat, the results are to be viewed with suspicion. The part relating to the importance of cleanliness in all dairy operations is also well treated.

The book has, however, been weakened by translation. The translators have aimed to produce a so-called popular book, and they have continually misused scientific terms. A calorie, page 117, is the amount of heat required to raise either *one pound* or *one kilo* of water 1°. On page 85, under the head, "Determination of Milk-sugar," the directions read "After it has been boiled for six minutes it is filtered through asbestos, and the reduction of the copper takes place spontaneously in the asbestos tube." On page 204, acidity is imparted to milk by either hydrochloric acid or soda. Fat, after saponification, is called butter. On page 284 condensed milk is called thickened milk. On page 224, a cut is given of a cheese mold, and it is called a cheese vat. On page 219, a curd knife is called a cheese vat. On page 81, an evaporating dish is called a thin porcelain basin.

The book should have been decreased in size, by omitting the obsolete parts and by a vigorous pruning of the cumbersome parts relating to the treatment of trivial matters.

HARRY SNYDER.

WATER AND PUBLIC HEALTH. BY JAMES H. FUERTES. New York: John Wiley & Sons. 75 pp. Price \$1.50.

Mr. Fuertes has brought together much valuable information, and his method of stating a large part of it in graphic form, renders it decidedly more serviceable. Long columns of figures cannot be digested without considerable mental effort, but a

coordinated chart strikes the eye at once. The very instructive illustration on page 7, showing the relations between "height of ground water," "extent of sewerage," and the "typhoid death-rate," could have been improved had the ordinates for the "ground water curve" been increased. Printed as it is, the scale is too small for easy reading.

Referring to the correspondence between an improved typhoid death-rate and the introduction of purer municipal water supplies, the author says, "other circumstances may have had something to do with this reduction, such as better care of the sick." This is true, but it could have been added that improvement in the typhoid rate not uncommonly antedates the sanitary betterments, because of the private purchasing of drinking water from other and purer sources.

The author forcibly presents the care exercised by European authorities in furnishing the consumers with water, either unpolluted or else improved to the greatest extent permitted by sanitary science; and he graphically illustrates what may be expected if Americans continue to use raw water from sources such as those whence many of our cities now draw their supplies.

The book is well worthy of a place in the library of every one interested in the water question, whether his interest be that of a citizen or of a specialist.

W. P. MASON.

ELEMENTS OF CHEMISTRY. BY RUFUS P. WILLIAMS. viii + 412 pp.  
Boston: Ginn & Co. 1897. Price, \$1.20.

Personal contact with twenty-five hundred pupils in chemistry and some experience in the preparation of text-books, have made it possible for the author of this work to prepare a book unusually free from erroneous statements. It resembles the "*Introduction to Chemical Science*," an earlier book by the author, but nearly all topics are treated with greater fulness, and the text is less marred by abbreviations. The experiments are numerous and suggestive. The illustrations are clear. The choice and arrangement of topics will not meet with universal approval. The number of laws and theories that are mentioned, and, in most instances, discussed, seems excessive for an elementary book that is intended chiefly for the use of high schools. After a brief account of oxygen, nitrogen, hydrogen

and carbon, follow descriptions of the manufacture of hydrochloric, hydrofluoric, nitric and sulphuric acids. The halogens and sulphur follow much later. Acids, bases, and salts are discussed in detail before any of the metals are studied.

The author justifies his method by pointing out the "enthusiastic interest" of his classes. Such evidence of its value should be criticised with caution.

The treatment of the metals is full and interesting. Two very brief chapters are given to organic chemistry, and an appendix contains the names of a few books of reference, lists of chemicals and apparatus, a few tables, and some directions for manipulation.

L. B. HALL.

HUMPHRY DAVY, POET AND PHILOSOPHER. BY T. E. THORPE, LL.D., F.R.S. The Century Science Series. New York: The Macmillan Co., Ltd. 1896. viii + 240 pp. Price \$1.25.

Professor Thorpe, of the Royal College of Science, London, is no novice in the writing of biographies of chemists; his "Essays in Historical Chemistry" (London, 1894) included sketches of Boyle, Priestley, Scheele, Cavendish, Lavoisier, Faraday, Graham, Wöhler, Dumas, Kopp, and Mendeléeff, and now chemists have to thank him for a very satisfactory biography of the illustrious Davy. The author had access to much original material not before used, private letters, and documents in possession of London scientific societies, notably the original records of Davy's experiments in the Royal Institution. The result is a more accurate work than that of Dr. Paris (1831) and less partial than that of Sir Humphry's brother John (1836). Professor Thorpe was fortunate in having a charming as well as distinguished personality for his subject, and he treats it very agreeably. He seems to have become inoculated somewhat with Davy's poetical nature for he writes of the "Pierian Spring," "Devotions to Calliope," the "Daring of Phaeton," and of "Priestley's Pegasus."

Davy's childhood and scanty education in youth are touched upon; he seems to have had no training in science, whatever, when he began work at Beddoes "Pneumatic Institution" in Bristol, but his industry and ability were inborn, and his discovery of "Laughing Gas" at the age of twenty-one started him on a career which reached a lofty height before he arrived at the age of thirty.

The portrait which serves as frontispiece is an unfamiliar one, being from a painting by Jackson, taken at the age of 45. Davy appears less handsome than in the portraits by Sir Thos. Lawrence, Lonsdale, and others. The book has an index. The next volume of the series will be on Michael Faraday, by Dr. Silvanus P. Thompson.

H. CARRINGTON BOLTON.

A HANDBOOK OF MODERN EXPLOSIVES. BY M. EISSLER. Second edition, enlarged. London: Crosby, Lockwood & Son; and New York: D. Van Nostrand Co. 1897. 8vo. 153 Figs. xx + 406 pp. Price \$5.00.

That there is a field for a book of this kind is shown by the fact that it has now gone to a second edition, the first edition having been published in 1890. In the preparation of this work the author has omitted all description of gunpowder, as it typifies the ancient explosives, and devotes his pages largely to nitroglycerine and gun cotton and the preparation made from them, though some space is given to the nitrosubstitution explosives and the proposed substitutes for gunpowder. The scope of the treatment covers not only the methods of manufacture, the apparatus employed and materials required, the tests of the raw materials and manufactured products, and the properties of the explosives produced, but much space is given to the methods of using them in the industries and in war, while a goodly number of pages are devoted to the Explosives Act of Great Britain and other official regulations. In fact the book is written wholly from the English standpoint as regards this industry. This new edition is revised and contains about one hundred more pages and fifty more illustrations than the first edition. The most substantial addition is a chapter on nitrogelatine and gelatine dynamite in practical applications, while sections have been added on the tests of ingredients and concentration of spent acids in the nitroglycerine manufacture; apparatus for measuring the strength of explosives; properties of frozen nitroglycerine compounds and other minor topics.

It is to be regretted that many obvious errors which occurred in the old edition have been repeated in this, while new ones have been added. One remarkable error is in the cuts illustrating the manufacture of nitroglycerine by Mowbray's Process. The authority cited for the description is Mowbray's "Trinitroglycerine." The three cuts given bear the legends "Mowbray's



Nitroglycerine Apparatus, etc." We have Mowbray's book before us but, although he gives an illustration of his apparatus opposite page 68, we do not find in this or any edition of Mowbray's work the cuts Eissler gives. These cuts occur in Hill's Notes on Explosives, and we have always understood that Hill devised this special form of apparatus though it was based on Mowbray's principle. Eissler repeats the statement that Sobrero discovered nitroglycerine in Paris, though Guttman has some time since announced that "It was expressly stated to me by the late Mr. Sobrero that he made his invention in Turin, where he was professor, and not in the laboratory of Pelouze," and that a sample of the original nitroglycerine is still kept at Avigliana. Throughout the book there is a carelessness in the use of scientific and especially chemical terms, sulphate of potassa and potassium nitrate, for instance, occurring in the same paragraph, while in the description of the methods of analyzing acids such typographical errors as  $180 \text{ BaSO}_4 = 42.06 \text{ H}_2\text{SO}_4$  are committed repeatedly.

The book contains much information and is useful, but it would have been a better book if the collated matter had been digested.

CHARLES E. MUNROE.

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### BOOKS RECEIVED.

Text-book of Physical Chemistry. By Clarence L. Speyers, Associate Professor of Chemistry, Rutgers College. 1897. New York: D. Van Nostrand Co. vii + 224 pp. Price \$2.25.

A Short Handbook of Oil Analysis. By Augustus H. Gill, S.B., Ph.D. Philadelphia: J. B. Lippincott Co. 1898. Cloth. 139 pp. Price \$1.50.

Introduction to Electrochemical Experiments. By Dr. Felix Oettel. Translated by Edgar F. Smith. Philadelphia: P. Blakiston, Son & Co. 1897. 144 pp. Price 75 cents.

Practical Exercises in Electrochemistry. By Dr. Felix Oettel. Translated by Edgar F. Smith. Philadelphia: P. Blakiston, Son & Co. 1897. 92 pp. Price 75 cents.

Electric Treatment in Gout and the Uric-acid Diathesis. By Robert Newman. Reprinted from the *Medical Record*, Dec. 11, 1897. New York: The Publishers' Printing Co. 16 pp.

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### ERRATUM.

In the last (January) issue of the Journal, p. 29, line 11, for the author's name read "H. D. Campbell" instead of "E. D. Campbell."



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### FIFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1897.

BY F. W. CLARKE.

Received January 27, 1898.

*To the Members of the American Chemical Society:*

During 1897 comparatively few new determinations of atomic weights have appeared. The data given are as follows:

*Carbon.*—Scott<sup>1</sup> has carefully studied the determinations of the atomic weight of carbon which depend upon the combustion of the element and the weight of the dioxide formed, and has discovered an important correction. This is due to the considerable change of volume in the potash solution produced by the absorption of carbon dioxide, which involves a notable change in the reduction of the weighings to a vacuum. Scott has measured the amount of this change, and has applied it to the work of his predecessors with the subjoined results. In each case the values given are the means of the several experiments recorded.

	Uncorrected.	Corrected.
Dumas and Stas .....	11.9975	11.9938
Erdmann and Marchand.....	12.0093	12.0054
Roscoe .....	12.0029	11.9973
Friedel .....	12.0112	12.0056
Van der Plaats .....	12.0031	12.0018
	<hr/>	<hr/>
Mean,	12.0048	12.0008

<sup>1</sup> *J. Chem. Soc.*, 71, 550, May, 1897.

These values are based upon  $O = 16$ ; with  $O = 15.879$ , the corrected mean result becomes  $C = 11.910$ .

Scott further criticises in detail the determinations by Stas which depend upon the combustion of carbon monoxide, and shows that they require possible corrections and involve various uncertainties. He concludes "that the atomic weight of carbon is by no means one of those most accurately known, and that a careful revision of it is imperative."

*Nitrogen, Chlorine, and Silver.*—Leduc<sup>1</sup>, on the basis of his density determinations, assumes  $N = 14.005$  when  $O = 16$ . Applying this to the determinations by Stas of the ratios  $Ag : Cl$ ,  $AgCl : O_2$ , and  $AgCl : NH_4Cl$ , he finds a discrepancy of about one part in 320. That is, the work of Stas gives  $N = 14.044$  instead of 14.005. This disagreement Leduc attributes to the presence of occluded oxygen, as pointed out by Dumas, in the silver used by Stas. For this he assumes a correction, and then, combining his value for nitrogen with the data given by Stas, he computes  $H = 1.0076$ ,  $Cl = 35.470$ , and  $Ag = 107.916$ . The correction applied by Leduc seems to be somewhat uncertain; and it is doubtful whether his determination of the density of nitrogen is entitled to greater weight than the other data which are involved in the calculations.

*Aluminum.*—In the third and fourth reports of this committee Thomsen's data for the atomic weight of oxygen are given. In these determinations oxygen and hydrogen were compared with aluminum as an intermediary; but the aluminum used was not absolutely pure. Had it been pure, the atomic weight of the metal, with reference to the two gases, could have been computed.

Thomsen now<sup>2</sup> gives the data necessary for the comparison, and deduces the atomic weight of aluminum. The impurities are determined, and corrections for them applied. There is also a correction for the change in volume of the potash solution in which the metal was dissolved. Applying the corrections, Thomsen finds that 0.99897 gram pure aluminum correspond to 0.11195 gram of hydrogen. Hence, with  $H = 1$ ,

$$Al = 26.770.$$

<sup>1</sup> *Compt. rend.*, 125, 299, August 2, 1897.

<sup>2</sup> *Ztschr. anorg. Chem.*, 15, 447.

Again, 0.99897 gram of metal is equivalent to 0.88824 gram of oxygen. Hence, with  $O = 16$ ,

$$Al = 26.992.$$

These two values, referring to the two standard units, are determined independently of each other, and are independent of any measured ratio between O and H. They are notably lower than the values computed by myself from Mallet's data, 26.91 and 27.11, and possibly should supplant the latter. This question, however, needs further discussion, and probably some additional experiments.

*Nickel.*—Atomic weight determined by Richards and Cushman,<sup>1</sup> from analyses of the anhydrous, sublimed bromide,  $NiBr_2$ . This substance is shown by the authors to be perfectly suited to the purpose of the investigation. The method of analysis was in all essential respects that used by Richards in other researches of the same kind, and was partly gravimetric and partly volumetric. On the one hand, the ratio  $2AgBr : NiBr_2$  was determined; on the other, the ratio  $2Ag : NiBr_2$ . All weighings were reduced to a vacuum. The results, in three series, were as follows:

## FIRST SERIES.

Weight $NiBr_2$ .	Weight $AgBr$ .	Atomic weight Ni.
2.26113	3.88769	58.646
2.80668	4.82431	58.708
1.41317	2.42880	58.716
1.71759	2.95307	58.650
2.48565	4.27357	58.651
4.32997	7.44280	58.700
2.18072	3.74856	58.693
		<hr/>
		Mean, 58.680

## SECOND SERIES.

Weight $NiBr_2$ .	Weight $AgBr$ .	Atomic weight Ni.
3.28039	5.63892	58.691
2.70044	4.64208	58.686
3.38230	5.81391	58.698
1.33459	2.29435	58.670
1.25054	2.14963	58.693
1.32778	2.27384	58.690
2.24452	3.85805	58.705
		<hr/>
		Mean, 58.690

<sup>1</sup> *Proc. Amer. Acad.*, 33, 97, November, 1897.

## THIRD SERIES.

Weight NiBr <sub>2</sub> .	Weight Ag.	Atomic weight Ni.
3.28039	3.23910	58.701
2.70044	2.66636	58.709
3.38230	2.33990	58.689
1.33459	1.31787	58.689
1.25054	1.23482	58.698
1.32278	1.30629	58.675
2.24452	2.21652	58.676
		<hr/>
		Mean, 58.691

From all these data the authors conclude that the atomic weight of nickel cannot be far from 58.69 when  $O = 16$ , or 58.25 if  $O = 15.88$ .

From series two and three 15.32086 grams of silver give 26.67078 grams of bromide. Hence the percentage of silver in silver bromide is 57.444, which agrees with the value 57.445 found by Stas. This is a good check upon the accuracy of the work.

*Cobalt.*—The atomic weight determinations by Richards and Baxter<sup>1</sup> are in all essential respects like those of nickel which have just been cited. The three series of data are as follows :

## FIRST SERIES.

Weight CoBr <sub>2</sub> .	Weight AgBr.	Atomic weight Co.
2.25295	3.86818	58.950
2.88763	4.95732	58.975
1.88806	3.24056	59.026
		<hr/>
		Mean, 58.984

## SECOND SERIES.

Weight CoBr <sub>2</sub> .	Weight AgBr.	Atomic weight Co.
1.33564	2.29296	58.975
2.58129	4.43095	58.998
2.84382	4.88135	59.009
1.83722	3.15368	59.000
2.68584	4.61046	58.996
3.18990	5.47607	58.982
2.88914	4.95943	58.997
2.32840	3.99706	58.987
1.91703	3.29053	59.010
		<hr/>
		Mean, 58.995

<sup>1</sup> *Proc. Amer. Acad.*, 33, 115, December, 1897.

## THIRD SERIES.

Weight $\text{CoBr}_2$ .	Weight Ag.	Atomic weight Co.
1.33564	1.31702	59.002
2.58129	2.54585	58.955
2.84382	2.80449	58.977
1.83722	1.81170	58.991
2.68584	2.64879	58.969
2.88914	2.84891	58.998
2.32840	2.29593	59.003
1.91703	1.89033	58.999
		Mean, 58.987

If  $\text{O} = 16$ ,  $\text{Co} = 58.99$ , as the outcome of all the series. If  $\text{O} = 15.88$ ,  $\text{Co} = 58.55$ . From the data in series two and three the percentage of silver in silver bromide is 57.446, while Stas gives 57.445. The last five experiments, which are the best, give 57.447. This check on the accuracy of the work is therefore satisfactory.

*Tungsten*.—The investigation by Hardin<sup>1</sup> is rather the scrutiny of a method than an attempt to accurately fix an atomic weight. Most of the determinations of the atomic weight of tungsten have been based upon analyses or syntheses of the trioxide; and this substance is now shown to be exceedingly untrustworthy as regards the measurement of this constant. Hardin has made sixty-four determinations with the trioxide, in seventeen groups or series, using material from various sources, and working under a great variety of conditions. The values found range from  $W = 183.51$  to  $W = 185.00$ , when  $\text{O} = 16$ , the average of all being 184.106. The same discordance appears upon comparing the results obtained by previous investigators, and it seems to be partly due to absorptions of tungsten or its oxide by the boat in which the reductions or oxidations were effected, and partly to the presence of nitrogen in the trioxide when the latter was prepared from ammonium tungstate. At all events, the method is unsuited to its purpose, and the atomic weight of tungsten needs thorough reinvestigation by means of other processes.

*Cerium*.—The atomic weight of this metal has been redetermined by Wyruboff and Verneuil,<sup>2</sup> upon material purified by

<sup>1</sup> This Journal, 19, 657, August, 1897.

<sup>2</sup> Bull. Soc. Chim. [3], 17, 679.

an elaborate process and with extreme care. From this material the oxide  $\text{CeO}_2$  was obtained perfectly white—a result in corroboration of the researches of Wolf and of Wing, but contrary to later investigators who have always found the substance to be more or less colored. The existence of a white oxide is also confirmed by the recent investigations of Moissan.<sup>1</sup>

The salt chosen for the atomic weight determinations was the sulphate,  $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{Aq}$ , a compound which is perfectly definite and stable, and which is easily obtained in a state of purity. At  $250^\circ$  it loses its water with facility, and up to  $500^\circ$  it undergoes no further decomposition. By ignition at a white heat,  $1500^\circ$  approximately, all sulphuric acid is expelled, and the pure oxide remains. The other hydrated sulphates of cerium are less manageable. The material studied was derived from three distinct sources, partly from monazite, partly from cerite; and the results attained confirm one another. The weights were as follows, but nothing is said as to their reduction to a vacuum. Probably the reduction was not made.

## FIRST SAMPLE.

Hydrous salt.	Anhydrous salt.	$\text{CeO}_2$ .
1.2385	0.9875	0.5977
1.2730	1.0148	0.6138
1.2030	0.9590	0.5794
1.5420	1.2295	0.7430

## SECOND SAMPLE.

0.9642	0.7685	0.4642
1.3260	1.0571	0.6389
1.1429	0.9112	0.5518
0.9072	0.7232	0.4372

## THIRD SAMPLE.

1.2114	0.9658	0.5840
1.2411	0.9894	0.5984

From these data the following atomic weights are derived, when  $\text{O} = 16$  and  $\text{S} = 32$ , cerium being regarded by the authors as a dyad, with the oxide obtained having the formula  $\text{Ce}_2\text{O}_3$ .

<sup>1</sup> *Compt. rend.*, 124, 1233.

## FIRST SERIES.

From per cent. $H_2O$ .	From " $Ce_2O_4$ " in hydrate.	From $Ce_2O_4$ in anhydrous salt.
92.84	93.08	93.16
92.65	92.88	92.95
92.65	92.64	92.63
92.85	92.74	92.70
<hr/>	<hr/>	<hr/>
Mean, 92.74	92.84	92.86

## SECOND SERIES.

92.49	92.55	92.56
92.69	92.72	92.73
92.76	93.17	93.30
92.66	92.77	92.80
<hr/>	<hr/>	<hr/>
Mean, 92.65	92.80	92.85

## THIRD SERIES.

92.75	92.84	92.87
92.68	92.88	92.93
<hr/>	<hr/>	<hr/>
Mean, 92.71	92.86	92.90
Mean of all, 92.70	92.83	92.87

The extreme variation is 0.75, which becomes 1.125 when cerium is regarded as a triad.

From the entire series of determinations, the salt  $Ce_2(SO_4)_3 \cdot 8Aq$  gives in mean 20.278 per cent. of water, and 48.205  $CeO_2$ . The mean percentage of  $CeO_2$  in the anhydrous sulphate is 60.467. From these data, with  $H = 1$ ,  $O = 15.879$ , and  $S = 31.83$ , the following mean values for  $Ce'''$  are deduced:

From percentage of water.....	$Ce = 138.14$
From $CeO_2$ in hydrated salt.....	$Ce = 138.35$
From $CeO_2$ in $Ce_2(SO_4)_3$ .....	$Ce = 138.42$

The mean of these is  $Ce = 138.30$ . With  $O = 16$ , this becomes  $Ce = 139.35$ .

These figures are adopted in the table at the close of this report, as being probably more trustworthy than the older determinations, but they are still subject to a good deal of uncertainty.

Still another investigation upon cerium is reported by Boudouard,<sup>1</sup> who, following Schutzenberger, fractionates the salts of the metal. His atomic weight determinations are made by ignition of the sulphate; but the values assigned to  $O$  and  $S$  are

<sup>1</sup> *Compt. rend.*, 125, 772.

not stated. By fractionation of the acetate he gets an oxide giving from  $Ce = 135.1$  to  $140.7$ . From fractionations of the sulphate he finds  $Ce = 133.0$  to  $138.75$ . Hydrogen peroxide precipitates an oxide giving  $Ce = 137.15$  to  $137.6$ , while the unprecipitated portion ranges from  $137.85$  to  $139.9$ . He concludes that the oxide of cerium is accompanied by small quantities of another earth of lower atomic weight.

Wyrouboff and Verneuil<sup>1</sup> criticise the work of Boudouard, and suggest that his high values for  $Ce$  are due to the presence of thoria, while the lower values are ascribable to the other earths of the cerium-yttrium groups. To this criticism Boudouard<sup>2</sup> replies, defending the purity of his material. He now states that his  $CeO_2$  was *white*. Wyrouboff and Verneuil<sup>3</sup> reiterate their objections, and show that the variations in successive portions obtained by Boudouard are irregular, sometimes high, sometimes low, and not systematic in one direction as they should be with material representing an orderly fractionation.

It is evident from the discussion thus summarized that Boudouard's figures relate to mixtures, and not to one earth, whatever the mixtures may be. They are therefore unavailable as determinations of a definite atomic weight. It may be suggested here that a careful scrutiny of the supposed  $CeO_2$  is necessary in order to prove that it is not contaminated by higher or lower oxides of cerium, and that it does not contain, like certain other oxides, occluded gaseous impurities. Until these questions have been settled, all atomic weight determinations based upon weighings of ceric oxide are uncertain.

*Gaseous Densities.*—Lord Rayleigh<sup>4</sup> has continued his investigation upon the density of the principal gases, and now gives data for  $CO$ ,  $CO_2$ , and  $N_2O$ . His results, air being taken as unity, are tabulated as follows :

Oxygen .....	1.10535
Atmospheric nitrogen, plus argon.....	0.97209
Nitrogen .....	0.96737
Argon.....	1.37752
Carbonic oxide .....	0.96716
Carbon dioxide.....	1.52909
Nitrous oxide .....	1.52951

<sup>1</sup> *Compt. rend.*, 125, 950.

<sup>2</sup> *Ibid.*, 125, 1096.

<sup>3</sup> *Ibid.*, 125, 1180.

<sup>4</sup> *Nature*, December 30, 1897. *Chem. News*, December 31.



Calculated from the density of CO, with  $O = 16$ ,  $C = 11.9989$ .

*Mathematical Relations.*—Rummel,<sup>1</sup> in a paper upon "The Spectra of the Alkalies and their Atomic Weights," works out a series of relations which seem to be significant. For the formulae developed, which are algebraic, the original paper must be consulted. When  $Na = 23$ , as the starting-point, the spectral relations give  $He = 3.64$ ,  $K = 39.05$ ,  $Rb = 85.15$ , and  $Cs = 133.47$ . These values are near enough to the actual determinations to show that the mathematical process deserves careful consideration.

*Miscellaneous Notes.*—At the Toronto Meeting of the British Association for the Advancement of Science, Brauner presented a paper on the atomic weight of thorium. Also at the Washington meeting of the American Chemical Society, Venable gave the preliminary results of an investigation upon zirconium. These determinations are as yet unpublished.

A memoir upon the atomic weight of molybdenum, by A. Vandenberghe, has been awarded the Stas prize of the Belgian Academy. It will appear in the quarto form adopted by the Academy for its more important publications.

The following table of atomic weights is essentially that given in Clarke's "Recalculation," a new edition of which was published by the Smithsonian Institution in January. The names of elements which represent changes from the table of 1896 are italicized.

	H = 1.	O = 16.
Aluminum .....	26.91	27.11
Antimony .....	119.52	120.43
Argon .....	?	?
Arsenic .....	74.44	75.01
Barium .....	136.39	137.43
Bismuth .....	206.54	208.11
Boron .....	10.86	10.95
Bromine .....	79.34	79.95
Cadmium .....	111.10	111.95
Calcium .....	39.76	40.07
<i>Carbon</i> .....	11.91	12.00
<i>Cerium</i> .....	138.30	139.35
Cesium .....	131.89	132.89
Chlorine .....	35.18	35.45
Chromium .....	51.74	52.14

<sup>1</sup> *Proc. Roy. Soc. of Victoria (Australia)*, 10, Part I, page 75.

	H = 1.	O = 16.
<i>Cobalt</i> .....	58.55	58.99
<i>Columbium</i> .....	93.02	93.73
<i>Copper</i> .....	63.12	63.60
<i>Erbium</i> .....	165.06	166.32
<i>Fluorine</i> .....	18.91	19.06
<i>Gadolinium</i> .....	155.57	156.76
<i>Gallium</i> .....	69.38	69.91
<i>Germanium</i> .....	71.93	72.48
<i>Glucinum</i> .....	9.01	9.08
<i>Gold</i> .....	195.74	197.23
<i>Helium</i> .....	?	?
<i>Hydrogen</i> .....	1.000	1.008
<i>Indium</i> .....	112.99	113.85
<i>Iodine</i> .....	125.89	126.85
<i>Iridium</i> .....	191.66	193.12
<i>Iron</i> .....	55.60	56.02
<i>Lanthanum</i> .....	137.59	138.64
<i>Lead</i> .....	205.36	206.92
<i>Lithium</i> .....	6.97	7.03
<i>Magnesium</i> .....	24.10	24.28
<i>Manganese</i> .....	54.57	54.99
<i>Mercury</i> .....	198.49	200.00
<i>Molybdenum</i> .....	95.26	95.99
<i>Neodymium</i> .....	139.70	140.80
<i>Nickel</i> .....	58.24	58.69
<i>Nitrogen</i> .....	13.93	14.04
<i>Osmium</i> .....	189.55	190.99
<i>Oxygen</i> .....	15.88	16.00
<i>Palladium</i> .....	105.56	106.36
<i>Phosphorus</i> .....	30.79	31.02
<i>Platinum</i> .....	193.41	194.89
<i>Potassium</i> .....	38.82	39.11
<i>Praseodymium</i> .....	142.50	143.60
<i>Rhodium</i> .....	102.23	103.01
<i>Rubidium</i> .....	84.78	85.43
<i>Ruthenium</i> .....	100.91	101.68
<i>Samarium</i> .....	149.13	150.26
<i>Scandium</i> .....	43.78	44.12
<i>Selenium</i> .....	78.42	79.02
<i>Silicon</i> .....	28.18	28.40
<i>Silver</i> .....	107.11	107.92
<i>Sodium</i> .....	22.88	23.05
<i>Strontium</i> .....	86.95	87.61
<i>Sulphur</i> .....	31.83	32.07
<i>Tantalum</i> .....	181.45	182.84

	H = 1.	O = 16.
Tellurium .....	126.52	127.49
Terbium.....	158.80	160.00
Thallium .....	202.61	204.15
Thorium.....	230.87	232.63
Thulium.....	169.40	170.70
Tin .....	118.15	119.05
Titanium .....	47.79	48.15
Tungsten .....	183.43	184.83
Uranium .....	237.77	239.59
Vanadium .....	50.99	51.38
Ytterbium .....	171.88	173.19
Yttrium .....	88.35	89.02
Zinc .....	64.91	65.41
Zirconium .....	89.72	90.40

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 26.]

## THE VOLUMETRIC DETERMINATION OF COBALT.<sup>1</sup>

By HARRY B. HARRIS.

Received January 14, 1898.

### INTRODUCTION.

**Z**INC, manganese, nickel, and cobalt constitute an analytical group of more than ordinary importance. The methods for the quantitative determination of these metals are mainly gravimetric. The volumetric methods applied in the estimation of zinc have won a permanent place with the analyst, and are used daily, where zinc determinations are of prime interest.

The estimation of manganese by means of potassium permanganate according to the recommendation of Volhard has almost completely supplanted the methods ordinarily used with that metal. When nickel and cobalt are brought to the front, and when the methods proposed at various times for their determination are carefully examined, it will be found that volumetric processes must be relegated to a very subordinate position.

Accurate, rapid, volumetric methods, giving satisfactory results for these two metals, would be welcomed by all analysts. It is true that volumetric methods have from time to time been brought forward, yet they seem not to have met with favor:

<sup>1</sup> From a thesis presented for the degree of Doctor of Philosophy, 1897.

at least they have not gained a permanent hold in the literature pertaining to analysis.

In the hope that perhaps a careful review of some of the proposed schemes for the volumetric determination of cobalt would disclose their inherent weakness with the discovery of modifications which would lead to their elimination and the improvement of the methods, the present investigation was undertaken. The review includes about every method which has been published upon the subject under discussion.

#### PREPARATION OF MATERIALS.

It seemed advisable not to use the ordinary salts of the market, but to derive the cobalt from some source after careful purification of the same.

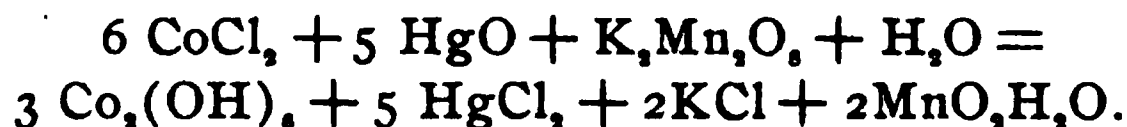
To this end, recrystallized, dry, and pure purpureo-cobalt chloride was reduced by means of purified hydrogen in a porcelain crucible. The bright metallic mass after cooling in hydrogen was transferred to a weighing bottle which was preserved in a vacuum desiccator. Portions of this purified metal were weighed off for the several determinations that were made.

#### REVIEW OF METHODS.

##### I. WINKLER'S METHOD.

In the *Zeitschrift für analytische Chemie*, 3, 420, Clemens Winkler called attention to the fact that potassium permanganate will oxidize cobaltous salts; although the precipitation of the cobaltic oxide is not in any sense complete unless there be simultaneously present some substance which will mechanically carry down the cobalt oxide formed.

The reaction was conceived to proceed in the sense of the following equation:



The purpose of the mercuric oxide is merely to mechanically separate the cobaltic oxide from the solution. The method seemed to be, in the main, very satisfactory.

As indicated in the equation, the salt used was the chloride. The oxidation is retarded by sulphuric acid, while even traces of other oxy-acids prevent it. The presence of organic sub-

stances is harmful, but ferric salts are without influence.

So far as can be determined from the various papers by Winkler upon this method, he operated in the cold. No mention is made of this point, although the succeeding work will prove that it is a matter of moment.

Indeed, it was observed when operating in the cold that when the point of complete oxidation was approached the solution frequently acquired a muddy appearance, and that the action of the permanganate was decidedly sluggish, consequently the end of the reaction was noted with difficulty.

In *hot* solutions, on the contrary, the end reaction was comparatively sharp and the pink color observed without great effort. In the trials made, the solution of the chloride was brought to boiling; the mercuric oxide was then introduced and the permanganate added, with frequent shaking of the containing flask. The precipitated mercuric oxide was found to be the most suitable, it being more efficient in the precipitation of the cobaltic oxide.

The mercuric oxide was preserved, according to the recommendation of Winkler, as an emulsion, and was so added as occasion demanded. Experience demonstrated that when the cobalt content of the solution was high, it was advisable to dilute it with water to one-half or even more. This facilitated and made more certain the reading of the end reaction. The permanganate usually consisted of about four grams of the pure salt dissolved in one liter of water. A solution of cobalt as chloride, containing 0.1334 gram, was first used.

When the analysis was conducted as outlined above, the following results were obtained:

	Gram.	Per cent.
1 .....	0.1332	99.85
2 .....	0.1329	99.62
3 .....	0.1323	99.17
4 .....	0.1332	99.85
5 .....	0.1338	100.30

These determinations were made in boiling solutions, and confirm the statement that in the cold the reaction is so slow that its conclusion cannot be sharply determined.

To verify this, the results which were gotten when operating

in the cold are introduced, the solution used containing 0.1334 gram cobalt as the chloride :

	Gram.	Per cent.
1 .....	0.1253	93.93
2 .....	0.1253	93.93
3 .....	0.1244	93.25
4 .....	0.1241	93.03

The cobalt content of the solution was reduced and a series of oxidations carried out in the same manner as before, observing every precaution.

With a cobalt solution of 0.0534 gram operating in *hot solution* the results were :

	Gram.	Per cent.
1 .....	0.0527	98.67
2 .....	0.0529	99.05
3 .....	0.0518	97.00
4 .....	0.0536	100.38
5 .....	0.0533	99.81

while in the cold there was obtained :

	Gram.	Per cent.
1 .....	0.0503	94.11
2 .....	0.0503	94.11
3 .....	0.0501	93.71
4 .....	0.0491	91.83

The cobalt content was now increased to 0.2668 gram with the following result in *hot solution* :

	Gram.	Per cent.
1 .....	0.2649	99.31
2 .....	0.2646	99.21
3 .....	0.2639	98.94

In *cold* solution :

	Gram.	Per cent.
1 .....	0.2375	89.02
2 .....	0.2357	88.36
3 .....	0.2369	88.80

Two facts are obvious in these results, the method is satisfactory and yields concordant percentage when it is carried out in hot solutions. It is also apparent that, as the quantity of cobalt is raised, the results do not approach the theoretical so closely.

As previously observed, the mercuric oxide was found efficacious in withdrawing the cobaltic oxide from solution. Other

reagents designed to perform the same function were tried ; thus, in using barium carbonate with a solution of 0.1334 gram cobalt, low end readings were obtained.

	Gram.	Per cent.
1 .....	0.0989	74.14
2 .....	0.0972	72.93
3 .....	0.0936	70.16

Ferric hydroxide was also applied, but it proved worthless.

In the well-known method of Volhard for the determination of manganese by means of potassium permanganate, zinc sulphate is added. With the cobalt salt this was without effect, and evidently for the reason that the action of the permanganate in the case of manganous and cobaltous salts is quite different.

In the first case there is formed an oxide of decidedly acidic character which tends to combine with oxides still present in the solution, and for this the zinc salt is well suited. Whereas in the cobalt salt the oxidation proceeds with the formation of a rather indifferent sesquioxide which must be mechanically carried down.

On using an emulsion of zinc oxide, the oxidation with potassium permanganate proceeded very slowly, the liquid also clarifying with difficulty.

However, on adding to the solution of cobalt chloride, containing zinc oxide, a solution of ferric chloride, the titrations advanced rapidly in hot solutions, and the cobaltic oxide settled out quickly ; this was no doubt due to the influence of the ferric hydroxide. As evidence of the value of the above procedure, the following results are appended :

	Theoretical cobalt. Gram.	Found cobalt. Gram.	Percentage.
1 .....	0.1334	0.1330	99.70
2 .....	0.1334	0.1328	99.55
3 .....	0.1334	0.1332	99.85
4 .....	0.1334	0.1336	100.15
5 .....	0.1334	0.1363	99.50
6 .....	0.1334	0.1363	99.50
7 .....	0.1334	0.1369	99.93
8 .....	0.1334	0.1362	99.42

Cobalt is quite frequently associated in minerals and ores with arsenic as well as with nickel. By the usual method of solution of such compounds, the arsenic, for example, would be

brought into the state of arsenic acid, and when in this condition it prevents the oxidation of the cobalt; when nickel is present it was thought that, by means of a double titration in presence of arsenic acid, the cobalt might be determined, but experiment proved the contrary.

Not infrequently copper is found associated with cobalt. How its presence would influence the determination of the latter by the method under discussion seemed of interest, and experiments with this end in view were instituted. The first solution operated upon contained 0.1370 gram of cobalt and 0.0125 gram of copper, and gave upon titration :

	Cobalt. Gram.	Per cent.
1 .....	0.1363	99.49
2 .....	0.1360	99.28
3 .....	0.1359	99.18

When the copper content was raised to 0.0500 gram, the cobalt found was

	Cobalt. Gram.	Per cent.
1 .....	0.1365	99.64
2 .....	0.1362	99.42
3 .....	0.1360	99.28

But on raising the copper to 0.1300 while the solution still contained 0.1370 gram cobalt there was found :

	Gram.	Per cent.
1 .....	0.0804	58.69
2 .....	0.0783	57.15
3 .....	0.0795	58.03

Recalling the fact that when ferric chloride was added to a solution of cobaltous chloride containing zinc oxide, the hitherto murky solution became clear, and allowed of a complete oxidation of the cobalt, the thought suggested itself that possibly the oxidation of cobalt salts in the presence of mercuric oxide would be complete in the cold, if ferric chloride was added, but experiment did not bear out the suggestion. 0.1370 gram of cobalt gave :

	Gram.	Per cent.
1 .....	0.1331	97.16
2 .....	0.1329	97.01
3 .....	0.1335	97.45



Lead is another metal which sometimes occurs associated with cobalt. In solutions of cobalt and lead the cobaltic oxide was almost quantitatively precipitated by potassium permanganate on addition of mercuric oxide and ferric chloride. A solution containing 0.1370 gram cobalt and 0.0120 gram of lead gave :

	Cobalt. Gram.	Per cent.
1 .....	0.1372	100.15
2 .....	0.1369	99.93
3 .....	0.1373	100.22

As the lead content is raised the results depart from the theoretical quite considerably.

In the presence of arsenic acid and ferric chloride the titration of cobalt can be made by means of potassium permanganate, using mercuric oxide to carry down the cobaltic oxide. With these conditions a cobalt solution of 0.1272 gram gave :

	Cobalt. Gram.	Per cent.
1 .....	0.1273	100.08
2 .....	0.1268	99.70
3 .....	0.1270	99.84

With antimony the remarkable observation was made that as the content of this metal was increased the determination of the cobalt became exact. A solution containing 0.1272 gram cobalt and 0.0900 gram of antimony gave on titration :

	Cobalt. Gram.	Per cent.
1 .....	0.1323	104.01
2 .....	0.1317	103.54
3 .....	0.1321	103.85

When the antimony was raised to 0.1700. while the cobalt content remained the same, the solution gave on titration :

	Cobalt. Gram.	Per cent.
1 .....	0.1297	101.97
2 .....	0.1289	101.33
3 .....	0.1304	102.52

But when 0.4400 gram antimony were present with 0.1272 gram of cobalt the results obtained were :

	Cobalt. Gram.	Per cent.
1 .....	0.1274	100.16
2 .....	0.1265	99.45
3 .....	0.1267	99.60

In this review of Winkler's method the conclusions reached are that the results are fairly accurate when the cobalt content is not too great, but that it can scarcely claim recognition as a trustworthy method under most conditions, and that it can in no wise be regarded as equal in value to the ordinary gravimetric methods employed in the estimation of this metal.

Winkler has asserted in the *Zeitschrift für analytische Chemie*, 7, 48, that the method is applicable in the analysis of a speiss holding arsenic and nickel, yet his own results seem to show that the conditions must be accurately known, otherwise the method is faulty.

Work done with these conditions shows that the determinations were least unsatisfactory when the cobalt stood to the nickel in the ratio of 1 : 2 ; but even then the results were always high.

## II. MCCULLOCH'S METHOD.

This method appeared in the *Chemical News*, Vol. 59, and, for its execution, requires the following salts for its execution : Potassium bichromate, ferrous ammonium sulphate, and a solution of potassium cyanide. In carrying out the method, the solutions of bichromate and potassium cyanide are brought together in a flask, the mouth of which is closed with a doubly perforated cork fitted with a thistle tube and an exit tube. A few drops of ammonia are added to the solution to neutralize any free acid which may be present, after which the liquid is boiled to expel the air from the flask.

There is next added the solution under examination, which must be hot, then the reaction occurs almost instantaneously and is complete. The cork carrying the thistle tube is no longer necessary.

An excess of a warm concentrated solution of ammonium chloride is now added and the whole boiled for a short time to drive off the excess of potassium cyanide. Nickel sulphate is now added and the cobaltic cyanide is precipitated.

The nickel sulphate also serves to decompose the potassium nickel cyanide which otherwise would combine with the ferrous ammonium sulphate subsequently introduced, with the consequent production of low results. The solution so precipitated is brought together with a known quantity of ferrous ammonium sulphate and after the addition of a few drops of hydrochloric acid it is titrated with potassium bichromate of known strength.

A solution of 0.1144 gram of cobalt when titrated as above, gave with these conditions (25 cc. potassium cyanide and 25 cc. potassium bichromate) :

	Cobalt. Gram.	Per cent.
1 .....	0.1032	90.21
2 .....	0.1039	90.82
3 .....	0.1014	88.64
4 .....	0.1000	87.41
5 .....	0.1023	89.42

When the quantity of potassium cyanide was reduced one half, the results obtained were :

	Cobalt. Gram.	Per cent.
1 .....	0.1056	92.32
2 .....	0.1030	90.04
3 .....	0.1000	87.41
4 .....	0.1060	92.67
5 .....	0.1022	89.32
6 .....	0.1004	87.85
7 .....	0.1009	88.20
8 .....	0.1022	89.32
9 .....	0.1015	88.72
10 .....	0.1020	89.15
11 .....	0.0995	86.97

From this series of results, obtained with the exercise of great care, it is obvious that the suggestion of McCulloch possesses little merit in the desired direction.

The wide divergence of these results from the theoretical and from each other, show that the method has defects.

III. FLEISCHER'S METHOD.

In the *Journal für praktische Chemie*, 110, 49, there is published by E. Fleischer a method intended for the separation of cobalt from nickel, and the subsequent volumetric determination of the separated cobaltic oxide.

The cobalt salt under examination is mixed with an excess of sodium hydroxide and then treated with a solution of sodium hypochlorite.

Both of these reagents are added in excess, as the complete oxidation of the two metals is of primary importance. The solution is brought to a boil and the black precipitate, consisting of the two sesquioxides, after settling, is filtered off and is then treated with a solution of ammonia (1 : 3).

On applying heat the nickelic oxide is reduced completely, leaving the cobaltic oxide unchanged; this is filtered off and brought in contact with ferrous ammonium sulphate and sulphuric acid, when the ferrous salt will be oxidized at the expense of the cobaltic oxide.

The unchanged ferrous salt is then determined by titration with potassium permanganate.

On working with a solution containing 0.1240 gram cobalt and 0.1263 gram nickel, the resulting sesquioxides were treated with dilute ammonia and boiled for a short period; it was then filtered and treated with ferrous ammonium sulphate and titrated as recommended, with the result that there was found :

	Cobalt. Gram.	Per cent.
1 .....	0.1730	139.52
2 .....	0.1730	139.52
3 .....	0.1729	139.44
4 .....	0.1730	139.52

With 0.0496 gram cobalt and 0.1263 gram nickel, following the method with care, I found :

	Cobalt. Gram.	Per cent.
1 .....	0.0620	125.00
2 .....	0.0619	124.86
3 .....	0.0627	125.98
4 .....	0.0651	131.25

With 0.1240 gram cobalt and 0.0506 gram nickel, there resulted :

	Cobalt. Gram.	Per cent.
1 .....	0.1407	113.47
2 .....	0.1400	112.90
3 .....	0.1350	108.07
4 .....	0.1384	111.61

But, on making up an ammoniacal solution of ammonia (sp. gr. 0.96), with three parts water, as recommended, and boiling for a longer period, the results were more concordant.

With a solution containing 0.0915 gram cobalt and 0.1263 gram nickel, there was found :

	Cobalt. Gram.	Per cent.
1 .....	0.0935	102.19
2 .....	0.0937	102.51

On lowering the nickel content to 0.0550 gram and submitting the oxides to the action of boiling ammonia for one hour, the results continued high.

	Cobalt. Gram.	Per cent.
1 .....	0.1097	119.89
2 .....	0.1094	119.56

When the period of boiling was extended to two hours, 0.0915 gram cobalt, in the presence of 0.1263 gram nickel, gave :

	Cobalt. Gram.	Per cent.
1 .....	0.0937	102.62
2 .....	0.0930	101.64

But when the nickel content was lowered to 0.0505 gram and the solution was boiled for two hours, the results were high :

	Cobalt. Gram.	Per cent.
1 .....	0.1048	114.53
2 .....	0.1035	113.11

These results show conclusively that the weakness of the method is in the reduction with ammonia. The proportion of the two metals is also shown to have an effect on the determination: the proportion of 2 cobalt to 1 nickel seemed especially unfavorable.

#### IV. DONATH'S METHOD.

In the *Berichte*, 1879, p. 1868, appears a method devised by Donath. It is really proposed as a modification of the Fleischer method. The instability of the sodium hypochlorite is a bar to its general acceptance, as is also the reduction by ammonia.

As a modification, Donath suggests the oxidation by iodine in a sodium hydrate solution, whereby the cobalt is completely converted into the sesquioxide state, while the nickel remains as

nickelous oxide. The precipitate may then be filtered off and the sesquioxide brought into a distilling apparatus along with hydrochloric acid, when the following reaction takes place :



The liberated chlorine is conducted into a potassium iodide solution and the liberated iodine is titrated by sodium hyposulphite.

From the iodine found the cobalt can be readily calculated.

On oxidizing a solution containing 0.1263 gram nickel and 0.1240 gram cobalt with thrice sublimed iodine, the results were always high, as the following series will show :

	Cobalt present. Gram.	Cobalt found. Gram.	Percentage.
1 .....	0.1240	0.1414	114.03
2 .....	0.1240	0.1426	115.00
3 .....	0.1240	0.1286	103.71
4 .....	0.1240	0.1240	100.00
5 .....	0.1240	0.1438	115.97
6 .....	0.1240	0.1388	111.93
7 .....	0.1240	0.1607	129.60

But on using chemically pure iodine the results were much closer :

	Cobalt. Gram.	Gram.	Per cent.
1 .....	0.1240	0.1261	101.69
2 .....	0.1240	0.1240	100.00
3 .....	0.1240	0.1235	99.60
4 .....	0.1240	0.1296	102.34
5 .....	0.0496	0.0480	96.57
6 .....	0.0496	0.0491	98.99
7 .....	0.0496	0.0478	96.16
8 .....	0.0496	0.0500	100.81

When the nickel content was reduced to 0.0506 gram with 0.1240 gram cobalt, the results were as follows :

	Cobalt. Gram.	Gram.	Per cent.
1 .....	0.1240	0.1243	100.24
2 .....	0.1240	0.1248	100.65
3 .....	0.1240	0.1236	99.76
4 .....	0.1240	0.1251	100.88

From these results it can be seen that the purity of the iodine is of prime importance, otherwise part of the nickel will be oxidized. The method may be considered as fairly accurate.

## V. VON REIS' METHOD.

In the *Zeitschrift für angewandte Chemie*, 1890, appears an article by M. A. von Reis and F. Wiggert on the determination of cobalt in the volumetric way.

The cobalt solution is treated with an emulsion of zinc oxide and brought to boiling, when a known quantity of a standardized solution of potassium permanganate is added.

The oxidized cobalt falls to the bottom and allows of the back-titration of the potassium permanganate by ferrous ammonium sulphate.

	Cobalt present. Gram.	Cobalt found. Gram.	Percentage.
1 .....	0.1334	0.1330	99.70
2 .....	0.1334	0.1325	99.32
3 .....	0.1334	0.1328	99.55
4 .....	0.1334	0.1334	100.00
5 .....	0.1334	0.1340	100.45

To all appearances this is by far the most satisfactory method yet proposed. Its simplicity recommends it.

## CONCLUSION.

After careful repetition of these methods, making varying conditions wherever deemed advisable, one is justified in concluding that none of them possess the degree of accuracy required in any trustworthy determination of cobalt. A good volumetric method for this purpose still remains to be devised.

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## RECENT WORK IN ENGLAND ON THE PURIFICATION OF SEWAGE.<sup>1</sup>

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**T**HERE are few questions connected with municipal government which cause as much trouble as the disposal of sewage in such a manner as to prevent any cause for complaint, and it is certainly not far from the truth to say that, at the present time, there is no large inland city in the world that has succeeded in satisfactorily disposing of the refuse matter that passes through the sewers.

<sup>1</sup> Read at the Washington Meeting, December 29, 1897.

The three methods used for the purification of sewage are: irrigation, or sewage farming; chemical precipitation; and intermittent filtration.

The first two methods have been tried by many large cities, and opinions differ as to their comparative merits. The history of sewage disposal is evidence of this difference of opinion.

There are in Great Britain forty-three cities which have a population of over 70,000. Direct information from personal investigation shows that, in 1897, twenty-one of these cities discharged their sewage practically untreated into tidal rivers, or into the sea: Liverpool, Edinburgh, Dublin, Belfast, Bristol, Newcastle, Hull, Portsmouth, Dundee, Cardiff, Oldham, Sunderland, Aberdeen, Brighton, Birkenhead, Swansea, Gateshead, Plymouth, South Shields, Middleborough, Cork, and Stockport; nine used chemical precipitation as a means of purification: London, Glasgow, Leeds, Sheffield, Bradford, Salford, Bolton, Huddesfield, and Southampton; two, chemical precipitation, allowing the effluent to pass over a small area of land: Manchester, 30 acres, and Burmley, 30 acres; five, broad irrigation: Leicester, Blackburn, Norwich, Preston, and Walsall; two, broad irrigation preceded by chemical precipitation: Birmingham and Wolverhampton; one used chemical precipitation for a portion of the sewage and broad irrigation for the remainder: Rochdale, chemical precipitation with 250,000 gallons and broad irrigation with 1,000,000 gallons. Of the German cities containing over 70,000 inhabitants, only Berlin, Breslau, Magdeburg, Frankfort, Danzig, Charlottenburg, Braunschweig, Halle, and Essen treat the sewage. Frankfort, Halle, and Essen by chemical precipitation, the other cities by broad irrigation, Berlin using for the purpose 14,473 acres and having in reserve 6,737 acres.

In all these cities there is great difficulty in obtaining satisfactory results. Those cities using broad irrigation find that more and more land must be added to the so-called sewage farm to prevent the drainage from causing a nuisance, and in those cities where the chemical precipitation method is employed, there is no doubt that there has been great difficulty in obtaining sufficient purification, especially when the surrounding district is extensively occupied, and where there is no large water-course to carry away the purified effluent. The question, there-



fore, that is now engaging the attention of sanitary engineers is, can that third process, intermittent filtration, be substituted in place of the other two?

The work that has been carried on at the Lawrence Experiment Station in regard to this third method of purification, is too well-known to all interested in the subject for me to dwell upon it, and I think it is only necessary to state that the experiments there carried out have shown that 100,000 gallons of crude sewage per day can be purified in the spring, summer, and autumn months by allowing it to filter through one acre of prepared sand filter-beds, underdrained at a depth of from three to five feet. In winter, however, where the filter-beds are unprotected from frost, snow, and ice, according to my observations, very much more than one acre of land is required for each 100,000 gallons. The top layer of sand becomes covered with a layer of what might be called *papier-mâché*, varying from one-eighth of an inch to almost a half inch in thickness. The formation of this layer is due to the finely divided paper in the sewage, and it is almost impervious to water. During the warm months, this coating is prevented from forming, by raking over the surface of the beds each week or two, but between the middle of November till the last of March in the cities of Massachusetts, this cannot be done and, as a rule, they are left untouched during this time. The rate of filtration gradually grows less and less, and from what I have seen at Gardner, Marlboro, Brockton, Framingham, and Westboro, I believe that twice, at least, and possibly four times as much area is required in winter as in summer.

This is a most serious defect in the process of intermittent filtration as recommended by the State Board of Health, of Massachusetts, and any improvement in the process which will partially obviate or remove this difficulty, either by reducing the amount of filtering surface required, so that covered beds could be used, or by preventing the finely ground paper from coming in contact with the filter-beds, so that the *papier-mâché* coating would not form, would be of great value. Such being the case I have been much interested in the recent developments in sewage treatment made in England, especially in the work of Dibden's bacteria filter now in use at Sutton, and in Cam-

eron's septic tank, now being tried at Exeter. Before speaking of these methods, however, I would like to say a word in regard to the filtering material used in Great Britain. Here sand is almost universally employed, there, on account of the difficulty of procuring sand of the desired quality, various other substances have been tried, burnt clay, or clay ballast, coke, breeze, cinders, clinkers, finely divided coal, etc., and it has been found that any jagged, porous substance is well fitted for the purpose, though curiously enough, experiments seem to show that either fine coal or fine cinders, are, on the whole, the best.

Regarding the special work that I have mentioned, Dibden's bacteria is the outcome of experiments made at Barking on the effluent of London sewage, the sewage itself being chemically treated with lime and iron sulphate.

In making the filtering at Barking the drains had been so arranged that by closing the valve of the main underdrain, the sewage could be kept in the bed for any number of hours, and a series of experiments were made with the view of ascertaining what would be the result of allowing the sewage to remain in the filter for a varying number of hours before passing it into the underdrains, the idea being that the work of purification was not limited to the surface, but took place throughout the body of the filter, and that a greater amount of purification could be obtained by filling the filter and allowing it to stand full for a certain length of time, thus giving the micro-organisms in the center and at the bottom of the bed the same amount of work to do as those nearer the surface, than by allowing the sewage merely to drain slowly through it. The method of working the bed was as follows :

The underdrains being closed, the filter was filled with dilute sewage which was allowed to remain in it for two hours ; the drains then being opened, the purified sewage was allowed to run off, air being drawn into the filter as the effluent ran out, the whole cycle requiring seven hours. The filling, standing, and emptying was constantly repeated for six days, when the work was stopped for twenty-four hours to allow of further aeration. The results obtained were most satisfactory. Running at the rate of 500,000 gallons per day, the albuminoid ammonia

was reduced from 0.712 part in 100,000 to 0.162, showing a purification equal to seventy-eight per cent. Running at the rate of 1,000,000 gallons per day, the purification, measured in the same way, equaled sixty-six per cent.

When both the amount treated and the percentage of purification are taken into account, this result is surprisingly good; yet the chief difference between these experiments and those that had been previously made, was that the whole of the filtering material was brought into intimate contact with the organic substance of the dilute sewage and allowed to remain in contact with it for a definite time, thus making full use of the cubical capacity of the filter.

The use in this way of the whole cubical capacity of the filter was new, and although it is only three years since these experiments were made, many sanitary engineers now claim that the cubical capacity of a filter should be taken into consideration in determining its purifying power and not only its superficial area, as has been the case. Therefore, instead of saying that one acre of filtering material three feet deep is capable of purifying so many hundred thousand gallons of sewage, one should say that the purification could be accomplished by 130,680 cubic feet of filtering material. Taking into account the depth of the filter as well as its area, is most important, for it leads to the possibility of purifying large amounts of sewage on comparatively small areas. The depth of the filter, however, must necessarily be limited to the point to which the air can be carried down in sufficient quantities for successful aeration, and as yet a sufficient number of experiments have not been made to decide how deep air can thus be carried, though undoubtedly the depth will be found to depend more or less on the filtering material that is used.

Sutton is the first town to attempt purifying its crude sewage by the above method, and as the plant is under the direction of Mr. Dibden and Mr. Thudicum, a detailed description of the filter and the results obtained, gathered by a personal visit to the works, may be of interest.

The population draining into the sewers is about 13,000, and the dry weather flow equals about 400,000 gallons per day. The sewage system is on the "separate" plan, rainfall being excluded,

yet during wet weather a large volume of subsoil water gains access to the sewers. The town contains few, if any, manufacturing establishments, and the sewage may be considered as a strong domestic sewage.

Sutton formerly purified its sewage by the use of chemicals and one of the precipitating tanks was utilized for the construction of a filter. On the floor of the tank, whose area was 183 square yards, was laid a six-inch drain, connected with nineteen lateral drains three inches in diameter. The main drain was provided with a six-inch valve so that the filter could be emptied or filled at will. The pipes were covered with very coarse, burnt clay, and upon this was placed a layer of burnt clay three feet deep, the smallest pieces of which could not pass through a half-inch mesh. The total capacity of this filter was 218 cubic yards, and when filled with burnt clay it would hold 13,500 gallons.

The crude sewage, after passing through iron screens to intercept large pieces of paper, is carried directly to the filter, the flow being stopped as soon as the sewage level reaches within an inch or so of the burnt clay. The time required for filling the filter is about one hour. The filter is allowed to remain full for about two hours, and then emptied, the time occupied in emptying it being one and one-half hours. The filter is then allowed to rest for two hours after which it is again charged. The effluent obtained is clear and without any strong odor, and appears to the eye equal to the best effluent obtained by the chemical precipitation process. From analyses made three or four times each month, from November, 1896, to June, 1897, and published in the *Surveyor* for July 9, 1897, the amount of purification as calculated from the albuminoid ammonia equals about fifty-eight per cent., while the amount of suspended matter is reduced from fifty to two and three-tenths grains per gallon.

The work of the filter compares favorably with the results obtained by many of the chemical precipitation processes, and, though twelve months is possibly too short a period from which to draw conclusions, the city is now constructing three more bacteria filters, and there seems to be no question that the above method leads one to entertain the view that with domestic sewage a purification equal to that obtained by chemical pre-

precipitation is possible with comparatively small, artificially prepared filters ; and from experiments which are now being made, it seems possible that some similar plan can be used with the sewage of a manufacturing city.

The effluent obtained by the bacteria filter when running at the rate of 1,000,000 gallons per acre, is not sufficiently pure to drain into a water-course, whose volume only equals or is less than the volume of the effluent, and when the stream runs through a thickly populated district as is the case in Sutton, and, consequently, there the first effluent is run through another filter of the same size and construction, filled however with burnt clay, all of which is small enough to pass through a half-inch mesh. The effluent from this second filter, at the time of my visit, was bright, clear, and without odor. The average amount of albuminoid ammonia in this effluent during the seven months from November to June was 0.243 part in 100,000 parts, the original sewage containing 1,130 parts, and the amount of suspended matter was reduced to 0.703 grain per gallon.

These results are certainly most interesting and instructive, and show what advance is being made in the process of purifying sewage by means of those micro-organisms which fulfil their life-functions in the presence of oxygen. Still more interesting than the bacteria filter on account of its being an entirely new departure, is the septic tank system of purification introduced by Donald Cameron, of Exeter, England. It has long been known that in the decomposition of organic matter by micro-organisms not a single species, but many species are at work and that they could roughly be divided into two classes : the putrefactive bacteria, those which live in the absence of light and oxygen and exercise a reducing or deoxidizing action, and those organisms whose life depends on the presence of oxygen and are known as the nitrifying bacteria. Mr. Cameron's septic tank treatment is based on the idea that the decomposition of organic matter is more easily and rapidly accomplished if the deoxidizing bacteria are allowed to do their work before the organic matter comes in contact with the nitrifying organisms. This is, of course, contrary to the commonly accepted idea that sewage is best treated before putrefaction begins, yet there is much to be said in favor of Mr. Cameron's plan. To separate the two

kinds of action the sewage is first led into a large tank, vaulted so as to exclude light and air, and is allowed to remain in this tank till putrefaction has taken place, when the sewage is passed upon the filter-beds which contain, as all filter-beds do, the nitrifying organisms. This method of treatment has been introduced into Exeter, England, and at present about 70,000 gallons are being treated each day.

The plant consists of the so-called septic tank, which is an underground tank built of cement concrete, sixty-four feet long, eighteen feet wide, and of an average depth of seven feet, having a capacity of about 53,000 gallons and of five filters made of coke breeze and furnace clinkers, about five feet in depth and covering all together an area of 400 square yards, having a capacity of 695 cubic yards. The crude sewage as it arrives at the plant passes through a railing to prevent large objects from entering the tank, while all small particles and solids in suspension pass freely to a grit chamber which is divided in two, each part having an inlet into the tank. The inlets are close to the bottom of the tank and the aperture of the inlet pipes is smaller on the tank side than on the sewer side, so that the sewage enters the tank with considerable force. The outlets are also beneath the surface of the water so as not to admit air or light, and so arranged that the water at the middle depth alone escapes. They are gauged so that the rate of flow may be measured; usually it is about 3,000 gallons per hour. The sewage from the septic tank is discharged simultaneously on two of the bacteria filters arranged according to Dibden's method. When these two filters are full they are emptied of their contents, and, while being emptied, the sewage from the tank passes on to others. The fifth filter remains idle one week, when it takes the place of the one that has longest been in use. Thus each filter remains idle one week out of every four. The filling and emptying of these filters is done automatically by an ingenious arrangement patented by Mr. Cameron and is said to be most satisfactory.

The action inside the tank is essentially of a putrefactive nature, no nitrates being formed. The organic matter is decomposed, or rather broken up into simpler forms, a large amount being rendered soluble, while at the same time ammonia and, I believe, free nitrogen are being formed. According to analyses

made by Dibden, the amount of oxidizable organic matter in solution is reduced about 30.8 per cent., the free ammonia about 26.9 per cent., the albuminoid ammonia about 17 per cent., and the suspended solids about 55 per cent. Pearmain and Moor, who have made a report on the process, state that there is no accumulation of sludge in the tank beyond a small amount of thin black sediment, which they report is so slight that a year's accumulation would scarcely be worth the trouble of removing. F. J. Commin, in a report on the process published in the *Lancet* for December, 1896, says that the deposit is very fine and inorganic, and that in a small tank after seven months' continual working and after quite 2,000,000 gallons of sewage had passed through the tank, the deposit was less than four inches over a surface of twenty-four feet by nine feet.

On top of the liquid in the tank there is a layer of flocculent matter from two to two and one-half inches in thickness, and from all accounts this seems to have been formed during the first few weeks that the tank was used and not to have increased much in thickness since that time. It appears to be composed of organic matter, formed I believe from the suspended matter in the sewage, and from all the information I have been able to obtain, it seems as though the organic matter in this flocculent layer was at first partially decomposed by the putrefactive organisms. Portions of it then sank to the bottom of the tank, where further action took place. Bubbles of gas collected around the fragments that had been carried down, causing them to rise to the surface and this process went on till the residue that remained at the bottom contained very little organic decomposable matter.

This action reminds one of what takes place in small streams into which sewage is emptied. I have often seen in such streams cakes of at least one-half yard in circumference rise from the mud at the bottom, and float down with the current.

According to Dibden the liquid that comes from the tank is of a brownish yellow color, offensive, and contains 2.73 grains per gallon of free ammonia, 0.175 grain of albuminoid ammonia, and the amount of oxygen absorbed from potassium permanganate in four hours is 1.405 grains per gallon. It contains no nitrates nor nitrites. The original sewage contained at the



same time 3.778 grains free ammonia, 0.212 grain albuminoid ammonia, and the oxygen absorbed from the potassium permanganate was 2.028 grains per gallon. This liquid is passed upon the filters as has been described and the effluent from these filters contains 1.705 grains free ammonia, 0.078 grain albuminoid ammonia, 0.253 grain nitrogen as nitrites, 0.353 grain nitrogen as nitrates, no suspended matter, and the absorbed oxygen from the potassium permanganate in four hours is only 0.388 grain per gallon.

The great advantage of the septic tank process, if it does what it appears to do, is that so large an amount of suspended matter is removed from the sewage that there will be very much less trouble with the clogging up of the surface of filter-beds in winter, and consequently an area that is large enough for the purification in summer will be more nearly, or possibly quite, sufficient for the work during the winter months.

It is also claimed that a large amount of the organic matter in solution is removed in the septic tank and if this is so, which appears probable from the analyses that have been made, it may not be too much to hope that future developments in this direction taken in connection with the using of the cubical capacity of a bacteria filter, may so reduce the area required for purification, that filter-beds may, without too great expense, be protected from snow and ice.

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## INVESTIGATION OF THE THEORY OF SOLUBILITY EFFECT IN THE CASE OF TRI-IONIC SALTS.

By ARTHUR A. NOYES AND E. HAROLD WOODWORTH.

Received January 20, 1898.

THE theory of the effect of salts on the solubility of one another has, in the case of di-ionic salts having one ion in common, been quite thoroughly tested and confirmed.<sup>1</sup> The solubility of tri-ionic salts in the presence of other salts, however, has been much less investigated. The theory of the phenomenon has, to be sure, been already developed, and has been partially tested by experiments with lead chloride in the presence of other salts.<sup>2</sup>

<sup>1</sup> Compare especially Noyes and Abbot : *Ztschr. phys. Chem.*, 16, 125.

<sup>2</sup> Noyes : *Ibid.*, 9, 626.



There was found, however, to be only an approximate agreement between the theory and the facts, probably because the dissociation-values involved are uncertain. Moreover, the theory could not be tested in the case where a salt with a common bivalent ion was added, probably owing to the fact that a double salt was formed. A further investigation of the subject seems therefore to be desirable.

To this end we have determined the solubility of lead iodide in pure water, and in potassium iodide and lead nitrate solutions of varying strengths. We made use of lead iodide because of its slight solubility (one molecular weight in about 600 liters); for, in such dilute solutions, the influence of the two substances on the dissociation of one another is hardly appreciable, and the tendency to the formation of double salts is ordinarily very slight,—two phenomena which often have a disturbing influence in concentrated solutions. In order to determine the solubility, we have measured the electrical conductivity of the saturated solutions, and subtracted from it the conductivity of the water or of the solutions before treating with lead iodide. This method has the advantage over the analytical determination, of greater convenience; and in this case it is especially well adapted, as it furnishes directly a knowledge of the concentration of the ions, so that it is not necessary to consider dissociation-values.

Two samples of each of the three salts were prepared by different methods. These samples were in all cases shown to be exactly alike as far as the conductivity of their solutions was concerned, which indicates that the substances were, in all probability, pure. One sample of the potassium iodide was prepared by treating the commercial, chemically pure salt with alcohol until it was about one-half dissolved, and by subsequent crystallization from this solution by evaporation. The other sample was obtained by crystallizing from water, the residue left undissolved by the alcohol. The lead nitrate was in one case obtained by crystallization of a commercial sample from water; in the other, by precipitation with nitric acid followed by crystallization from water. One sample of lead iodide was prepared by metathesis from lead acetate and potassium iodide; the other, by dissolving a commercial preparation in a strong potassium iodide solution, and then diluting with water. In

both cases the salt was purified by crystallizing twice from water. The solubility determinations were carried out as follows: Small forty-cc. glass-stoppered bottles were charged with an excess of the solid lead iodide and with pure water or with solutions of lead nitrate or potassium iodide; the stoppers were coated with paraffin, and the bottles rotated for five hours in a thermostat by means of a previously described apparatus.<sup>1</sup> The solutions were then allowed to settle for a short time, and blown out by means of a wash-bottle arrangement into a resistance cell of the Arrhenius type; and the conductivity was measured in the usual way.<sup>2</sup> All the solubility determinations and conductivity measurements were carried out at 25°. In all cases, duplicate determinations of the solubility were made in such a way that the condition of saturation was approached from both sides—that of supersaturation and that of undersaturation. Moreover, in order to make certain of the purity of the lead iodide, not only were the two different samples used, but each sample was also treated with successive amounts of water, and the conductivity of the corresponding solutions determined. A complete agreement was found to exist.

The following tables contain the specific conductivities (multiplied by  $10^{-7}$ ) expressed in Siemens' units. In all cases the conductivity of the water used (which was equal to  $9 \times 10^{-7}$ ) has been subtracted.

#### CONDUCTIVITY OF WATER SATURATED WITH LEAD IODIDE.

	I.	II.	III.	IV.	Mean.
Undersaturated . . . .	4016	4016	4023	4030	4021
Supersaturated . . . .	4039	4041	4042	4041	4041

#### CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS SATURATED WITH LEAD IODIDE.

Concentration of potassium iodide = 0.003077 equivalent per liter.		0.003000 equivalent per liter	
Undersaturated.    Supersaturated.		Undersaturated.    Supersaturated.	
I .....	6174                      6184	5316                      5343	
II .....	6172                      6200	5310                      5335	
Mean .....	6173                      6192	5313                      5339	

*Ztschr. phys. Chem.* 9, 600

*Ztschr. phys. Chem.* 2, 554.

CONDUCTIVITY OF LEAD NITRATE SOLUTIONS SATURATED WITH LEAD IODIDE.

Concentration of the lead nitrate	=0.003077 equivalent per liter.		0.002000 equivalent per liter.	
	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.
I .....	6807	6783	5798	5800
II.....	6791	6799	5796	5784
III.....	6799	6802	....	....
Mean .....	6799	6795	5797	5792

A consideration of the results in the tables shows that the comparable values agree closely with one another, although the determinations were carried out with different salts and at different times. The supersaturated solutions were, to be sure, about a half per cent. higher than the undersaturated, except in those experiments where lead nitrate was used, in which case they were practically equal. In the calculations described below, of the corresponding concentrations of the ions, the mean of the supersaturated and of the undersaturated values is always used.

In the following tables, the specific conductivities of the pure potassium iodide and lead nitrate solutions are given. In the upper half are the conductivities of the freshly-made solutions, and in the lower half those of the same solutions, after they had been rotated for the same time and under the same conditions as prevailed in the solubility experiments.

CONDUCTIVITY OF THE POTASSIUM IODIDE AND LEAD NITRATE SOLUTION BEFORE TREATMENT WITH LEAD IODIDE.

	Potassium iodide solution.		Lead nitrate solution.	
	Equivalents per liter = 0.003077	0.002000	0.003077	0.002000
First solution .....	4247	2809	3782	2498
Second solution ...	4257	2807	3785	2497
Mean.....	4252	2808	3784	2498
First solution.....	4288	2836	3771	2487
Second solution.....	4288	2849	3774	2487
Mean.....	4288	2843	3773	2487

In order to ascertain the conductivity of the dissolved lead iodide in the presence of the other two salts, we have subtracted the mean values in the lower half of this table from those of the saturated solutions in the two previous tables, it being assumed that the conductivity at these dilutions is an additive property. That this assumption is approximately correct may be concluded

from the fact that the lead nitrate and the potassium iodide at a dilution of 500 liters are 93.6 and 98.5 per cent. respectively dissociated, while at a dilution of 325 liters they are 92.0 and 96.9 per cent. respectively dissociated; in other words, the degree of dissociation is so great, and changes so little with increasing concentration, that it cannot be appreciably affected by the presence of the relatively small amount of lead iodide ions. In order now to derive the corresponding concentrations of the ions from the conductivity values, it is only necessary to divide the latter by the molecular conductivities of the respective salts at infinite dilution. We take as the values of the rates of migration, those calculated by Bredig, namely  $K = 70.6$ ,  $I = 72.0$ , and  $NO_3 = 65.1$ . The value for the lead ion has, so far as we know, not as yet been derived. Franke<sup>1</sup> has, to be sure, measured the conductivity of lead nitrate in dilute solution, from which the rate of migration can be calculated. Since, however, this value is for our purpose of fundamental importance, we thought it advisable to confirm the accuracy of his determinations by measurements of our own. We have therefore determined the conductivity of both of our samples of lead nitrate at different dilutions. Our values (represented by  $\mu_1$  and  $\mu_2$ , the mean value by  $\mu$ ), together with those of Franke ( $\mu_{Fr}$ ), are given in the following tables.

## EQUIVALENT CONDUCTIVITY OF LEAD NITRATE.

$V$ .	$\mu_1$ .	$\mu_2$ .	$\mu$ .	$\mu_{Fr}$ .
256	120.8	120.9	120.9	122.2
325	122.6	122.8	122.7	....
500	124.9	124.8	124.9	....
512	125.2	125.3	125.3	125.9
1024	128.2	127.7	128.0	127.1

As is seen, the conductivities of our two samples agree almost completely with each other, and also fairly well with those of Franke. To obtain the value at infinite dilution, we make use of Bredig's<sup>2</sup> extrapolation-values, which have been derived from a consideration of a large number of salts. The values, extrapolated in this manner from our measurements, are, for the three dilutions, 256, 512, and 1024 liters, 132.9, 133.3, and 134.0, re-

<sup>1</sup> *Ztschr. phys. Chem.*, 16, 471.

<sup>2</sup> *Ibid.* 13, 198.

spectively. We therefore take the mean, 133.4, as the value of the conductivity of the lead nitrate at infinite dilution.

Since the rate of migration of the  $\text{NO}_3$  ions is equal to 65.1, that of the lead ion must be 68.3, from which it follows that lead iodide has for its value at infinite dilution 140.3. Finally, the value derived for potassium iodide at infinite dilution from the above given rates of migration is 142.6. Now, if the corresponding specific conductivities are divided by these limiting values, we obtain the concentrations of the ions which correspond to the conductivity measurements given above. The results of these divisions are presented in the following table, those in the case of the lead iodide being placed under the heading "Found."

CONCENTRATION OF THE IONS IN THE SATURATED SOLUTIONS.

Potassium iodide ions.	Lead iodide ions.		Lead nitrate ions.	Lead iodide ions.	
	Found.	Calculated.		Found.	Calculated.
0.00	0.002873	.....	0.00	0.002873	.....
0.001969	0.001770	0.001731	0.001872	0.002358	0.002369
0.002982	0.001351	0.001296	0.002837	0.002155	0.002175

It is readily seen from these numbers that the solubility in the potassium iodide solutions as well as in those of the lead nitrate, is considerably less than in pure water, and further that the diminution caused by equivalent amounts of the two salts is quite different. We will now compare quantitatively the experimental results with the requirements of the principle of solubility effect.

The laws of mass action require that in the case of a saturated solution of a tri-ionic salt, the product of the concentration of the bivalent ion into the square of the concentration of the univalent ion shall be a constant quantity, whatever other salts may be present at the same time.<sup>1</sup> In this case the equation,

$$\text{Pb} \times (\text{I})^2 = \text{a constant},$$

should hold, where the chemical symbols denote the concentrations of the respective ions.

If  $m_0$  is the solubility of lead iodide in pure water,  $m$  its solubility in a potassium iodide or lead nitrate solution whose concentration is  $n$  (all expressed in equivalents), and  $a_0$ ,  $a$ , and  $a_1$ , the corresponding dissociation values, the following equation applies in the case where lead nitrate is present:

<sup>1</sup> *Ztschr. phys. Chem.*, 9, 627.

$$(ma + na_1) m^3 a^3 = m_0^3 a_0^3,$$

and where potassium iodide is present this equation:

$$ma (ma + na_1)^2 = m_0^3 a_0^3.$$

The value  $m_0 a_0$ , the concentration of the ions in the saturated solution in pure water, is found to be 0.002873; and the values of  $na_1$ , the concentrations of the ions in the lead nitrate and potassium iodide solutions in the four solubility experiments, are given in the first and fourth columns of the last table. From these we have calculated the values of  $ma$  (the concentration of the lead iodide ions) by the two formulas given above. This cubic equation is easily solved by substituting an estimated value of  $ma$ , and calculating the value of the left member of the equations, repeating this process until the value thus found becomes equal to  $m_0^3 a_0^3$ . The theoretical values obtained in this way are found in the last table under the headings "calculated."

The agreement between the experimental and the theoretical values, although not complete, is however entirely sufficient to prove the essential correctness of the solubility principle. The deviations are, in the case of the lead nitrate, 0.9 and 0.3 per cent., and in that of the potassium iodide, 4.1 and 2.2 per cent. It is however to be considered that the values of  $ma$  were not directly measured, but were obtained as the differences of two larger experimentally determined values, whereby the percentage error is greatly increased. In order to give an idea of the existing error relations, it may be mentioned that an error of one-half per cent. in the conductivity of the lead nitrate solution saturated with lead iodide, and an equal error in the subtracted conductivity of the pure lead nitrate solution, would cause in the value  $ma$  an error which would probably amount to 1.3 per cent. in the 0.003077 normal solution and 0.9 per cent. in the 0.002000 normal solution. Equal errors in the potassium iodide experiments would cause errors of 2.0 and 1.0 per cent. respectively in  $ma$ . It is therefore seen that the method cannot furnish very accurate results, and that the differences between the actual and the calculated values are not improbably due to experimental errors.

It has therefore been established by this investigation within

the (somewhat wide) limits of experimental errors, that *the solubility of lead iodide is diminished both by potassium iodide and by lead nitrate in such a way that the product of the concentration of the lead ions into the square\* of the concentration of the iodine ions remains constant.*

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
JANUARY, 1898.

## GLUCOSE IN BUTTER.<sup>1</sup>

By C. A. CRAMPTON.

Received January 22, 1898.

I have been unable to find, in the literature of food products or of food adulteration, any reference to the use of glucose or other form of sweetening material in butter. The nearest approach to it is the mention of starch by some of the German authorities as among the possible adulterants. In domestic practice, however, the addition of sugar to butter for purposes of preservation is doubtless almost as old as the art of butter-making itself, sugar and salt being the standard household preservatives for food products from time immemorial. But the use of sugar in this way is comparatively rare, salt being universally preferred as a preservative for this food product as it is for most products of animal origin. Sugar appears in several of the various U. S. Patents for so-called "improving" or renovating processes for butter, being added to it along with salt, saltpeter, and, in some cases, sodium carbonate. The sugar is usually in small quantity in these formulas, perhaps an ounce to eight pounds.

Within the past few years glucose has been used in butter specially prepared for export to tropical countries, as the West Indies or South America. The hot climate of these countries renders its preservation very difficult. It is usually put up in tins and various means are resorted to by the dealers in different nations who export to them for preventing the decomposition of their goods before they reach the consumer. Very large quantities of salt are used by the French exporters. I give below the figures obtained from the analysis of two samples of French butter, as exported, the one to Brazil, the other to the Antilles:

<sup>1</sup> Read at the Washington meeting, December 30, 1897.

	No. 2436. Butter "a la Morlaix" as exported to Brazil.	No. 2437. Butter "a la Morlaix" exported to the Antilles.
Water .....	10.29	10.19
Curd .....	1.24	1.31
Ash ..	10.29	10.06
Fat.....	78.18	78.44
	<hr/> 100.00	<hr/> 100.00

Figures for Fat.

Specific gravity at 40° C .....	9107	9112
Koettstorfer value.....	227.2	227.3
Reichert-Meissl figure .....	28.4	29.4

Chemical antiseptics, borax, salicylic acid, etc., are sometimes used, but the method found most efficacious by exporters in this country, so I am informed, is to use glucose in conjunction with a moderately heavy salting. I give below the figures obtained from two samples prepared in this way and exported to Brazil. One of these, No. 2443, has traveled twice across the equator and remained in my refrigerator since its return last August. While it is not exactly attractive to taste or smell, it is still possible to remain on speaking terms with it, which seems to be pretty good evidence of the effect of the glucose upon its keeping qualities.

I have inserted here also the analysis of a sample of so-called *beurre rouge*, or red butter, as exported to Guadeloupe. This is a very peculiar compound, highly colored, and contains large quantities of salt and glucose.

	No. 2434. Butter exported from the United States to Brazil.	No. 2443. Butter exported to Bra- zil and returned to the U. S.	No. 2460. <i>Beurre rouge</i> exported to Guadeloupe.
Water .....	16.29	18.93	21.60
Curd (N × 6.25).....	1.19	1.06	0.81
Ash.....	7.00	6.19	16.42
Fat .....	72.16	69.67	51.15
Glucose (by difference) .	3.36	4.15	10.02
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Figures for Fat.

Specific gravity at 40° C.	9093	9090	9080
Koettstorfer value.....	225.4	225.5	228.1
Reichert-Meissl figure..	27.2	25.4	26.4

Through the kindness of a firm of butter exporters I obtained



a sample of butter as purchased by them in western markets, and a sample of the same butter prepared for export by admixture of glucose, salt, and coloring-matter.

Following are the results obtained from these samples :

	No. 2445. Butter pur- chased in wes- tern markets.	No. 2446. Same pre- pared for export by admixture with glucose and salt.
Water .....	10.97	17.03
Curd(nitrogen $\times$ 6.25).....	1.31	0.94
Ash .....	2.56	8.49
Fat.....	85.08	70.59
Glucose (by difference) .....	0.00	2.95
	<hr/> 99.92	<hr/> 100.00

Figures for Fat.

Specific gravity at 40° C .....	9114	9110
Koettstorfer value .....	228.4	227.9
Reichert-Meissl figure .....	29.6	29.4

I also obtained a sample of the glucose used. It is the heavy, low converted sirup known as confectioners' glucose. It contained 16.5 per cent. of water, and gave  $[a]_D = 119.3$ ;  $R = 43.10$ .

The detection of glucose in butter presents no difficulty. In making the analysis of a butter containing it by the ordinary method of extracting the fat with ether, weighing the residue, incinerating and determining the curd by the loss on ignition, the presence of the glucose would be manifest by an abnormally high curd, as both would be burned off together. This is shown by the figures obtained in this way for curd in the four samples given above, as compared with the results obtained from the nitrogen determination. In the case of 2445, containing no glucose, the results by the two methods closely agree.

Number.	Percentage of curd obtained by usual method.	Percentage of curd obtained by (N $\times$ 6.25).
2434	4.55	1.19
2443	5.21	1.06
2445	1.39	1.31
2446	3.89	0.94
2460	10.83	0.81

In making a direct demonstration of the presence of glucose, I have used the method of washing it out with hot water, in the

manner first recommended by Wiley for the direct estimation of salt in butter and now used by the Association of Official Agricultural Chemists as an official method. Ten grams of the butter are weighed out in a beaker, transferred with hot water to a separatory funnel, where it is treated with successive portions (twenty to thirty cc.) of hot water, and the resulting solution made up, when cooled, to 250 cc.

A slight reduction of copper by this solution must not be taken as a qualitative proof of the presence of glucose in the butter, being due to the small amount of milk sugar present or perhaps to a reducing action by some of the albuminoids. Any considerable precipitation of Fehling's solution, however, may safely be ascribed to the presence of glucose or sugar, and the copper oxide reducing strength of the solution can be readily ascertained. The optical rotation may also be determined, the solution being readily clarified by means of alumina cream or by acid mercuric nitrate solution. The determination of salt can, of course, be made in the same solution, if desired.

In the previous analyses I have given the percentages of glucose as calculated by subtracting the sum of the water, ash, and fat from 100. The figures obtained in this way are not very exact, as the ether removes some of the glucose with the fat, making the figure for the latter too high, and for the former too low. I give below the percentage of glucose in each sample on the assumption that the same kind of glucose was used in Nos. 2434, 2443, and 2460, that I know to have been used in No. 2446, and calculating the figures from both the reducing and rotatory power.

Number.	Percentage of glucose calculated on basis of reducing power.	Percentage of glucose calculated on basis of rotatory power.
2434	5.57	5.64
2443	6.50	6.45
2446	5.10	5.24
2460	13.58	13.30

The relative quantities of butter, salt, and glucose used in No. 2446 were given to me by the manufacturer, as follows: 712 pounds of butter, 50 pounds of salt and 55 pounds of glucose. This would make the content of glucose 6.70 per cent. but it is apparent that considerable water was added as well.

Evidently the direct figures obtained above are much nearer the truth than the results obtained by difference. If the composition of the glucose is not known it could probably be worked out by the formula of Brown, Morris, and Millar.<sup>1</sup>

Butter No. 2443 was condemned by the customs authorities in Brazil, not on account of the presence of glucose, which seems to have escaped the notice of the analyst entirely, but on account of the low figures obtained from the fat, upon which was based a decision that it contained oleomargarine. The Reichert figure is low, but not sufficiently so, in my opinion, to justify the assertion that it was not butter fat. It is not to be presumed that the addition of the glucose would have any influence upon the fat, and the figures obtained in the case of Nos. 2445 and 2446 seem to prove conclusively that it does not.

I have had but few opportunities to examine domestic butters for the presence of glucose and have not found it as yet in any of the samples at hand. Its presence would be most likely, of course, in butters which had been subjected to reworking or renovation. In addition to its preservative action, the glucose probably acts mechanically to hold the large water content of the butter, enabling it to retain more than it otherwise would.

I will not attempt to discuss here the question as to whether or not the addition of glucose to butter constitutes an adulteration. It might be said to admit of some argument, however, as there does not seem to be any good reason, except custom, for preferring salt to sugar as a preservative for butter. Such butter could hardly be considered as coming within the scope of the national law known as the "Oleomargarine Law" as it would in no sense answer the definition of oleomargarine in that law.

DISCUSSION: *G. E. Patrick*.—I should like to know how the author accounts for the very great difference between the figures obtained in the glucose by incineration and that obtained by the direct method.

*C. A. Crampton*.—By the faulty method of fat determination, I have no doubt the ether takes out some glucose.

*G. E. Patrick*.—Would not petroleum ether be a better solvent?

<sup>1</sup> *Chem. News.*, 75, 42.

*C. A. Crampton.*—The suggestion seems to be a good one. I have no doubt it would dissolve less glucose.

In reply to Mr. Elworthy, who stated that butter was now preserved in India on a large scale by the addition of salt only, in hermetically sealed cans, and kept for six or seven months, and who asked whether the figures given were for dry glucose, Mr. Crampton said that the glucose was calculated on the supposition that the same kind of glucose, "confectioners' sirup," had been used in all cases.

### A METHOD FOR DETERMINING THE RESISTANCE OF ELECTROLYTES.

By PARKER C. MCILHINEY

Received January 22, 1904.

THE method commonly used for determining the resistance of an electrolyte is that of Kohlrausch, in which the resistance to be measured is made one arm of a Wheatstone bridge, while the current is an alternating one supplied by an induction coil and the balance is determined by a sensitive telephone instead of the galvanometer used in ordinary measurements. It is a zero method capable of a high degree of accuracy, but it is not very rapid and readings can not be taken at short intervals of time.

The method to be described does not lay claim to so high a degree of accuracy, as it is limited by errors in a galvanometer and by changes in the electromotive force of a battery during an experiment, but it is believed to have some advantages in the possibility of making many readings in a short space of time.

It consists briefly in determining by a galvanometer, preferably a d'Arsonval, the potential difference between the ends of a known resistance placed in series with the resistance to be determined. The current is supplied by a gravity battery and before passing through the electrolyte it is transformed into an alternating current by means of a rotary pole changer, but the current passing through the known resistance is direct.

When a current passes through two resistances in series the potential in each of them is proportional to its resistance.

Fig. 1, let  $R$  be a known resistance,  $R'$  be another known resistance, which may be replaced by the unknown resistance  $X$ .

Let  $f$  be the fall of potential in  $R$ , when  $R'$  is in series with it.  
 Let  $g$  be the fall of potential in  $R$ , when  $X$  is in series with it.  
 Let  $E$  be a constant electromotive force.

Then

$$f = \frac{RE}{R + R'} \dots\dots\dots (1)$$

and

$$g = \frac{RE}{R + X} \dots\dots\dots (2)$$

from which we get

$$X = \frac{(f - g)R + fR'}{g} \dots\dots\dots (3)$$

If we determine the fall of potential in  $R$ , when  $R'$ , the other known resistance is in the series, then replace  $R'$  by  $X$ , the unknown resistance, and again determine the fall of potential, we shall be able, by substituting in (3), to determine the value of  $X$ . If  $R$  be supposed equal to 0 equation (3) becomes

$$\frac{fR'}{g} = X \dots\dots\dots (4)$$

or

$$g : f :: X : R' \dots\dots\dots (5)$$

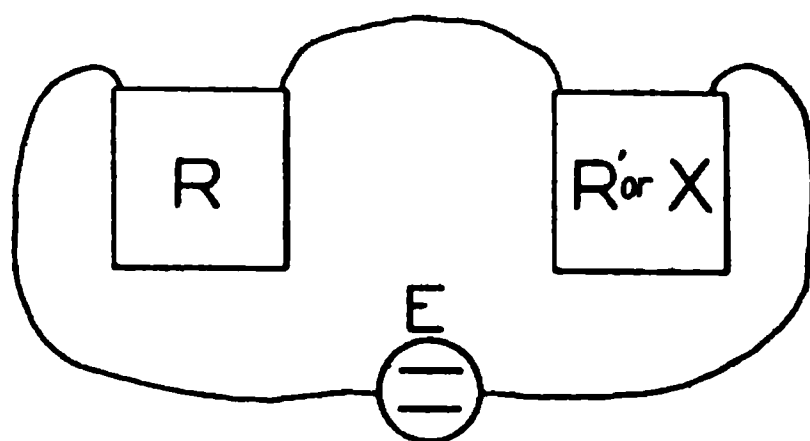


Fig. 1.

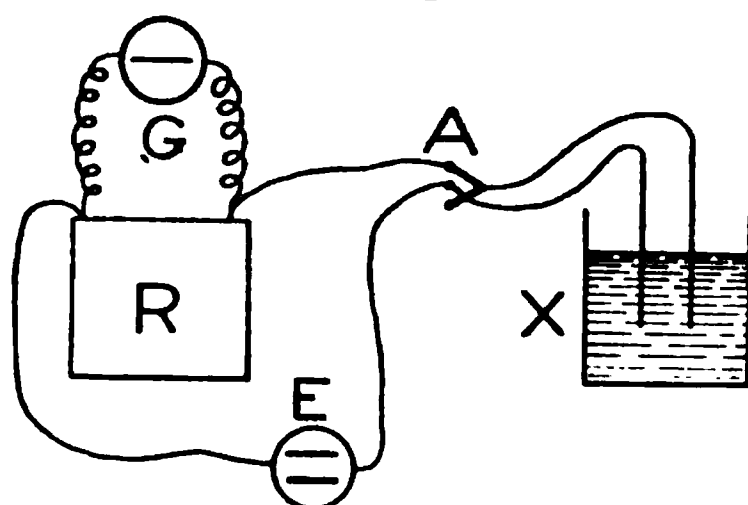


Fig. 2.

If  $R$  is very small in comparison with  $R'$ , equation (5) may be assumed to be applicable without the introduction of serious

error and the fall of potential in R would then always be proportional to the conductivity of R'.

If the measurement of the fall of potential in R is made by a d'Arsonval galvanometer, which gives readings proportional to the electromotive force of the current passing through it, and R is made small in proportion to R', the readings of the galvanometer give directly the conductivity of the electrolyte.

The method was devised to determine the resistance of silicates and similar substances under the influence of heat and for this purpose many readings had to be made. It proved well adapted to the purpose and probably would be convenient for other experiments in which a great many readings are desired from the same sample.

The apparatus necessary, aside from the containing vessel for the electrolyte and connecting wires, consists of two resistance boxes, one having small resistances, the other preferably containing resistances of the same order of magnitude as the quantities to be determined, a d'Arsonval galvanometer and a rotary pole changer to convert the direct current from the battery into an alternating one, so as to prevent polarization. The pole changer is a simple machine driven very well by any small motor which gives a fairly regular rotation. The method of connecting the apparatus is shown in Fig. 2.

R is the small resistance box.

X is the electrolyte.

E is a gravity battery.

A is the rotary pole changer.

G is the galvanometer.

The deflection of the galvanometer may be brought to a convenient figure for accurate reading, no matter what value X may have, by altering the value of R. The resistance of the galvanometer must be known, in order to make the calculation. Part of the current coming to the terminals of R passes through the galvanometer, and hence the resistance of the two together is slightly less than that of R alone. If we call the resistance of the galvanometer S, then the resistance of R and S together =

$\frac{R S}{R + S}$ . Here if R is small enough in proportion to S the con-

ductivity of the galvanometer may be neglected, and if  $R$  is changed to obtain a deflection more suitable for reading, the two readings may, without sensible error, be assumed proportional to the two values of  $R$ .

Changing  $R$  of course changes the sensitiveness of the whole arrangement and this may be done to as great an extent as the coils in  $R$  will allow. If it contains coils of one-tenth to twenty ohms the sensitiveness may be varied two hundredfold by a change in plugs, an operation requiring only a few seconds. In the work on heated silicates the resistance varied with the temperature from a comparatively small figure to practical infinity and the method made its determination quite simple, particularly as the same galvanometer was used for determining conductivity and for determining temperature by the thermoelectric method. Alternate readings of temperature and conductivity were taken at intervals of some seconds during the cooling of the materials from a high temperature by the use of a suitably disposed double switch.

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## THE COMMERCIAL ANALYSIS OF BAUXITE.

BY WM. B. PHILLIPS AND DAVID HANCOCK.

Received January 5, 1898.

THE bauxite mined in Georgia and Alabama, constituting practically all of the domestic supply, is used for the manufacture of alum and aluminum, in the proportion of about three-fourths to one-fourth. The analytical methods hitherto employed have been based, to a considerable extent, upon the purposes to which the material was applied.

It is obvious that the easy solubility of the alumina in sulphuric acid is a great desideratum for the manufacturer of alum, and furthermore, that the acidulated mass should filter readily, and be capable of rapid washing.

But it is generally impracticable for the ordinary chemist to base his methods on factory tests, for the reason that these are, for the most part, unknown to him. All that can reasonably be required of him is that his methods should not yield results widely at variance with those obtained on a large scale in actual operations.

Were the question of bauxite analysis one solely of the total amount of alumina, almost any of the methods used for the estimation of this substance in the presence of silica, oxide of iron, and titanitic acid could be employed. But the total amount of alumina is of secondary importance as compared with its ready solubility in sulphuric acid, in the manufacture of alum.

Whatever may be said as to the requirements of the manufacturers of aluminum, it is certainly necessary in the manufacture of alum that sulphuric acid should readily dissolve the alumina. One might go a step further and allow that the residue after treating with acid should be of such nature as to permit of rapid and thorough washing. This latter consideration, however, is not of such vital importance in the valuation of bauxite as that the material should dissolve readily in the acid, and that no substance deleterious in alum-making should at the same time go into solution. It seems to us that there are four main points to be considered in valuing bauxite by analysis for alum-making. Ranging them in the order of their relative importance they are as follows :

1. Easy solubility of the alumina in sulphuric acid.
2. Rapid filtration.
3. Rapid washing.
4. Freedom from substances that on going into solution would affect the quality of the alum, or other products.

There may be, of course, a difference of opinion as to the relative importance of the second, third, and fourth considerations but there can be no doubt of the rank of the first.

If the bauxite is ferruginous, the fourth point may come second, but at present and for some time to come the purer bauxite alone will come into the market. There is very little demand for second grade material, and while the percentage of ferric oxide is to be held in view in valuing even the pure bauxite it is not of much importance for the reason that it is generally very small.

The Georgia-Alabama bauxite consists of the trihydrate of alumina,  $\text{Al}_2(\text{OH})_6$ , or  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , mixed with clay, and what may prove to be a lower hydrate of alumina, possibly  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ .

There are three well recognized hydrates of alumina—the monohydrate (diaspore),  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or  $\text{Al}_2\text{O}_3(\text{OH})_3$ , containing



	Per cent.
Alumina .....	85.02
Water .....	14.98

the dihydrate,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  or  $\text{Al}_2\text{O}(\text{OH})_2$ , with

	Per cent.
Alumina .....	73.94
Water .....	26.06

and the trihydrate (Hydrargillite, Gibbsite), with

	Per cent.
Alumina .....	65.41
Water .....	34.59

The formula for bauxite,  $(\text{AlFe})_2\text{O}(\text{OH})_2$ , given by Roscoe and Schorlemmer<sup>1</sup> does not seem to apply to the American material. Assuming for the present that the domestic bauxite is a mixture of alumina trihydrate, clay, and possibly a lower hydrate, the methods adopted for its analysis, so far as concerns the alum-maker, should be based upon the estimation of two different things: (1) the amount of alumina existing as trihydrate, and very readily soluble in sulphuric acid, and (2) that existing as some other compound, whether a lower hydrate, or clay, less soluble in the acid, but which in the process of manufacture can be utilized. It would appear that the more easily soluble alumina should have a higher value placed upon it than the other. It costs less to make alum of material easily soluble than of material difficultly soluble, and if there exists in bauxite two or more alumina compounds, differing markedly from each other in solubility, the consumer is entitled to know what are the proportions between them.

Heretofore the analytical methods adopted, outside of factories, for the valuation of bauxite, have resulted in giving practically all of the alumina, and no efforts have been made, so far as known to us, to discriminate between the alumina compounds present.

The two methods ordinarily used are the Pittsburg, worked out by Mr. Jas. O. Handy, and the Spence method. Both of these agree in evaporating the mixture of sulphuric acid and bauxite to fumes of the so-called sulphuric anhydride and continuing the heat for some minutes. Mr. Handy recommends a mixture of

<sup>1</sup> Treatise on Chemistry, 2, [1], 444.

hydrochloric acid of 1.20 sp. gr., nitric acid of 1.42 sp. gr., and sulphuric acid of 1.20 sp. gr., in the respective ratio of 1 : 3 : 6. Mr. Spence uses a mixture of equal parts of strong sulphuric acid and water. In each case the ratio between acid mixture and bauxite is the same ; viz., one gram bauxite and 5 cc. acid. In using either method, taking up the residue in water, boiling, filtering, and washing thoroughly, very little alumina will be found in the residue. From numerous analyses we have found that considerably less than one per cent. of alumina is left in the residue, so that it may be said that practically all of it is dissolved.

More or less objection has been urged by alum-makers, to these methods. They have claimed that for their purposes the yield of alumina is too high, that by carrying the analytical treatment to fumes, whether using the mixture of acids, or sulphuric acid alone, compounds of alumina, which are not suited for the manufacture of alum, are decomposed and dissolved, and consequently the percentage of alumina does not represent what may fairly be considered as soluble alumina.

Aside from manufacturing processes, upon the discussion of which we do not enter, the objections seemed reasonable, and we began a series of investigations on commercial bauxite, not so much with the purpose of studying the exact composition of this material as of ascertaining whether a practical method of discriminating between the several compounds of alumina present in bauxite could be worked out. The results reached are extremely interesting and important alike to the shippers and the consumers, for they seem to indicate that it is perfectly feasible to determine the alumina existing as trihydrate, and therefore readily soluble, and the alumina as clay, or as a lower hydrate, and of less solubility.

From a lot of about 300 pounds of bauxite taken from the loading shed of a company actively engaged in mining and shipping for alum works, five separate samples were taken.

- A. A general average of the whole lot, lump and fine.
- B. A white, friable material, with no iron stains.
- C. A compact, cream-colored variety, with conchoidal fracture and pearly luster.

D. A variety full of nodules considerably stained with iron.

E. A clay, probably halloysite.

A separation of these varieties by elutriation was not possible, as they gave the following specific gravities :

	Sp. gr.
B .....	1.77
C .....	1.74
D .....	1.74
E .....	1.76

Two grams of A, through a sixty-mesh sieve, were treated with ten cc. sulphuric acid of 50° B., in a steam-bath at 100° C., for the time given below, 100 cc. water added, and the contents of the flask heated in the bath for ten minutes. It was then filtered, and washed thoroughly with hot water.

	Per cent.
Alumina extracted in two hours .....	53.37
“ “ “ one hour .....	53.18
“ “ “ one hour .....	53.21
“ “ “ one-half hour .....	51.27

The other samples were similarly treated for one hour. None of the solutions contained titanous acid, and only a small percentage of iron oxide was dissolved.

The insoluble residues were dried at 100° on tared filters, and weighed, then ignited and weighed again, the difference being taken as combined water. The amount of water combined with the alumina dissolved was ascertained in two ways :

1. By deducting the weight of the insoluble residue, dried at 100° from the total weight of substance taken, and, from this result, deducting the sum of the weights of alumina, ferric oxide, and moisture.

2. By deducting from the total loss on ignition the amount of combined water in the insoluble residue, and moisture.

The first method is probably more nearly correct.

The results of the analyses are as follows : .

SOLUBLE PORTION.					
	A.	B.	C.	D.	E.
Moisture .....	0.70	0.38	0.94	0.56	0.45
Ferric oxide .....	0.93	0.21	0.21	0.96	0.20
Alumina .....	53.21	58.03	58.94	48.69	3.11
Combined Water (1st method).....	28.28	30.78	31.00	25.77	1.87
“ Water (2nd method).....	28.17	31.14	31.31	25.90	1.05
“ Water (mean of 1st and 2nd). ..	28.23	30.96	31.15	25.83	1.46
“ Water (calculated) .....	28.20	30.75	31.26	25.80	1.64

## INSOLUBLE PORTION.

Combined Water .....	1.79	1.10	0.91	2.59	12.83
Alumina.....	4.15	2.69	2.39	7.48	37.70
Silica.....	7.28	3.06	2.40	8.85	42.88
Titanium oxide.....	3.63	3.70	3.08	4.82	1.10

These results point strongly to the formula  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , or  $\text{Al}(\text{OH})_3$ , for the substance dissolved. The iron is probably in the hydrated condition. If so, this would introduce a small correction, which however would be partially compensated by slight action on the clay residue, which will be mentioned later on. The figures for the soluble part have been verified in every case by duplicates, and in some cases by many analyses; as for instance in E, where it becomes very difficult to obtain accurately the per cent. of water, owing to the large amount of insoluble residue.

Little can be said as to the composition of the insoluble residue, but these results and many others which do not properly belong to the present discussion, seem to indicate that it consists chiefly of a halloysite or kaolinite clay; and that the larger portion of the titanium exists as the hydrated oxide, either titanous or metatitanous acid; that it also contains variable amounts of quartz or silicious sand; and it is not improbable that corundum and rutile are present in minute amounts, though neither have been identified with certainty.

The valuable constituent beyond a doubt is aluminum trihydrate, and the most reasonable settlement of the commercial question, it seems, would be to make this the basis of sales in the future. It might be argued that the alumina yield would be larger in this case than the analysis would indicate, as ordinary treatment will remove some alumina from clay.

To arrive at a fair conclusion in regard to the matter, it would appear to be necessary to further limit and define the word "bauxite" as applied to the Georgia-Alabama mineral. If the results given in this paper prove anything, they certainly show that in the so-called bauxite there is a sharp line of division as regards chemical action under certain conditions.

In outlining this work originally, it was intended to treat samples at various degrees of temperature, with various strengths of acid, the samples also to vary in their state of subdivision.

Other work has however prevented this, but enough has been done to throw some light on the question here involved. Acid of 40° B. dissolves practically the same per cent. of alumina as acid of 50° B. The substance passed through a sixty-mesh sieve gives the same per cent. of soluble alumina, as when all is passed through a 100-mesh sieve.

Some results have already been given showing difference in time of treatment. All results obtained indicate that if any of these variables of time, temperature, strength of acid, or subdivision be taken in regularly increasing increments, the per cent. of alumina dissolved increases rapidly at first and soon becomes fixed, the ratio  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  being unaffected, and afterwards the per cent. of alumina increases again, the ratio then approaching  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

Clearer proof could hardly be desired that bauxite, as we know it, is a mixture, and not a true chemical compound. The same result exactly would be obtained if workmen were directed to mix clay and the mineral, and the chemical methods now in use would not detect the change, at least only partially. They would show a lowering of the per cent. of alumina and increase of silica, but in nothing like the true amount of the addition, while a determination of  $\text{Al}_2(\text{OH})_6$  would detect it absolutely.

In order to establish the method on a scientific basis it is required to prove (1) that all alumina existing as  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  is extracted and (2) that it is contaminated by alumina from no other source.

Samples A and E were used for this purpose, the alumina being first extracted in the usual way using two grams of substance and fifteen cc. of 50° B. sulphuric acid at 100° C. for one hour, the residues washed free of alumina and dried at 100°, re-treated in the same way, etc.

Percentage of soluble alumina.		
	A.	E.
First extraction.....	53.18	3.21
Second " .....	0.22	1.20
Third " .....	....	1.08

Certainly no considerable amount of  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  could have remained or it would have appeared in the second extraction of A, but it seems that the reagent decomposes clay slowly as is shown

by E and it is probable that the additional alumina in A comes from the clay of the residue. It is intended at some time in the future to ascertain the minimum strength of acid which will extract at  $100^{\circ}$  C. in one hour all  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , and it is possible that the action on clay may become very slight and a correction be determined and applied.

Results are quite close enough for commercial purposes, and, while it is possible that they may vary three- or four-tenths or even five-tenths of one per cent. from the true figure for alumina existing as  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , the error is always in the same direction, and when the process is carried out in exactly the same way each time, results are remarkably concordant.

As illustrating this the following results are given ; they were made as checks on per cent. of soluble alumina.

	A.	B.	D.	E.	D.
1	53.21	58.03	58.94	48.69	3.11
2	53.18	58.00	59.05	48.80	3.12
3	53.14	58.10	59.00	....	3.08
4	53.26	....	....	....	....

It should be noticed that the error of the determination will depend upon the amount of the residue. A bauxite of average composition would give about twenty per cent. of insoluble residue, and the soluble alumina would probably be 0.25 per cent. too high, and the calculated  $\text{Al}_2(\text{OH})_6$  about 0.35 per cent. too high.

We beg, therefore, to recommend that, instead of carrying the analytical treatment to fumes of so-called sulphur trioxide, there be substituted the treatment with  $50^{\circ}$  B. sulphuric acid at  $100^{\circ}$  C. for one hour. We give at the conclusion of this paper our method of analysis. It may be of interest here to give some comparative results by the different methods.

A bauxite, containing by the Pittsburg method 59.20 per cent. of soluble alumina, was found by our method to contain 57.22 per cent. Another sample with 56.26 per cent. of soluble alumina by the Pittsburg method gave by our method 53.38 per cent.

A sample with sixty per cent. soluble alumina by the Pittsburg method gave us fifty-nine per cent., another with 54.87 per cent. gave us fifty-three per cent. Speaking generally we have found

that the difference between the Pittsburg method, or the Spence, and our method is less the purer the bauxite. This result may be anticipated, for the purer the bauxite the more of the alumina does it contain as the trihydrate.

Under the proposed change in the method of valuing bauxite it would be necessary to fix upon some name for the alumina dissolved at  $100^{\circ}$  by sulphuric acid of  $50^{\circ}$  B., and for that dissolved at fumes. We suggest the term "free alumina" for the alumina dissolved at  $100^{\circ}$  C. and "combined alumina" for the difference between this and the alumina dissolved at fumes, the sum of the two to be known as "available alumina." For instance, if a bauxite contained fifty-four per cent. of alumina soluble in  $50^{\circ}$  B. acid in one hour at  $100^{\circ}$  C. it would contain fifty-four per cent. of free alumina. If by the Pittsburg or the Spence method there was found fifty-eight per cent. "soluble alumina," we would now call this fifty-eight per cent. of "available alumina," and there would be four per cent. of "combined alumina."

There is an objection to this system of nomenclature in that the free alumina is really combined, just as much so as the additional alumina extracted by fuming acid. It being combined with water in the form of the trihydrate, the exact meaning of the term should be that the free alumina is the alumina from the trihydrate, and easily soluble in sulphuric acid. This much may be taken as proved. We can not state, at present, in what form the alumina exists that we propose to call "combined alumina." It may be as clay, as a lower hydrate, or as a form of  $\text{Al}_2\text{O}_3$  itself, insoluble except in fuming acid. It does not greatly matter in what form it exists, the chief thing to be considered being that it is not soluble in  $50^{\circ}$  B. sulphuric acid at  $100^{\circ}$  C., but is soluble in acid brought to fumes.

It is not in the province of this paper to assign exact commercial values to the free and the combined alumina, or to the free and the available alumina, as this should be left to the decision of the miners and the consumers. In the fertilizer trade it has not been found difficult to agree upon the price of water-soluble phosphoric acid, and available phosphoric acid, this latter being the sum of the soluble and the reverted. Acid phosphate

is now offered in bulk at so many cents per unit of available phosphoric acid, and the higher the percentage of the available acid the higher the price per unit.

We propose to introduce into the alum trade a system which has been used for many years in the fertilizer trade, and which has been found to be extremely useful. In bauxite the difference between the easily soluble trihydrate, and the difficultly soluble alumina in the residue, should be considered.

We are convinced that the changes proposed would be for the benefit of all concerned. Take for instance the case of a shipper who is sending out bauxite containing clay, such as E, and we beg to say again that E was taken from a lot of bauxite ready for shipment. If the prepared bauxite should contain an undue proportion of E, with only 3.11 per cent. of free (or easily soluble) alumina, it goes without saying that its value for alum-making would be seriously impaired. Comparing E with C (and both varieties came from the same bag) E has 3.11 per cent. of free alumina, and C has 58.94 per cent; in the insoluble portion E had 37.70 per cent. of alumina, and C had 2.39 per cent. In other words the free alumina in E was 7.62 per cent. of the total alumina, and in C it was 96.10 per cent.

Take another instance. With the very best bauxite there occurs a white clay which, when the material is ready for shipment, can not be distinguished from the bauxite itself. It may be mixed with the bauxite in considerable proportions and yet fail of recognition, because its physical qualities so nearly approximate those of pure bauxite. In the pits the lines of separation between bauxite and clay are perceptible indeed to the trained eye, but it is practically impossible to prevent the miners from overrunning the line. This is both theoretically and practically true. The situation at the mines renders it theoretically impossible to keep the clay out of the bauxite, and samples of clay picked out of the bauxite already mined show that it does occur in it. In pure bauxite the proportion of clay is at the minimum when the mine is operated from the middle of a big pocket of bauxite, but as the mining nears the sides of the pocket and approaches a bed of clay, the danger of admixture of clay increases, and when the pocket is almost exhausted and the mining is carried on close to the clay, more or less of this sub-



stance is sure to get in. The quality of the Georgia-Alabama bauxite is sufficiently high, as proved by the low silica and high free alumina, to preclude the possibility of there being much clay in it, but some clay is always present so far as our observation goes, covering several years.

We have ourselves obtained samples of these clays from the bauxite mines. One of them came from immediately next to a pure bauxite. It contained 41.80 per cent. of total alumina, of which 2.08 per cent. was free, 37.75 per cent. combined, and 1.97 per cent. insoluble. Of the total alumina 4.97 per cent. was free and easily soluble, 90.31 per cent. was 'combined' and difficultly soluble, and 4.72 per cent. was insoluble in fuming acid.

Another sample gave 43.00 per cent. of total alumina, of which 3.00 per cent. was 'free,' 37.40 per cent. 'combined,' and 2.60 per cent. insoluble. Of the total alumina 6.97 per cent. was 'free,' 86.98 per cent. was 'combined,' and 6.05 per cent. was insoluble.

Compare these results with those obtained from sample E, remembering that these two were clay taken from the mines, and E is clay taken from bauxite already mined. For convenience of reference we will call the two clays F and G, and put the comparative results in a table.

TABLE I.—CLAYS.

Sample.	Free alumina.	Combined alumina.	Available alumina.	Insoluble alumina.	Total alumina.	Total alumina = 100.			
						Free.	Combined.	Available.	Insoluble.
E.	3.11	35.45	38.56	2.25	40.81	7.62	86.86	94.48	5.52
F.	2.08	37.75	39.83	1.97	41.80	4.97	90.31	95.28	4.72
G.	3.00	37.40	40.40	2.60	43.00	6.97	86.98	93.95	6.05

Now take three good bauxites :

TABLE II.—BAUXITES.

A	53.21	3.55	56.76	0.60	57.36	92.76	6.19	98.95	1.05
B.	58.03	2.29	60.32	0.40	60.72	95.57	3.77	99.34	0.66
C.	58.94	2.04	60.98	0.35	61.33	96.10	3.32	99.42	0.58

The analyses show very clearly that treatment with sulphuric acid to fumes dissolves alumina from such clays as occur with

and in bauxite, and that treatment with acid at 100° C. does not dissolve this alumina. As regards bauxite itself the treatment at 100° C. serves to discriminate between the alumina of the trihydrate and the alumina of clay, or of a lower hydration.

As to calcining the bauxite before shipment in order to remove the water of hydration, we do not think it advisable. In well arranged bauxite plants the material is now heated in revolving cylinders to remove hygroscopic water, but the temperature should not be great enough to cause loss of combined water. In order to test the effect of loss of combined water on the solubility of the alumina at 100° C. we selected a very pure variety of bauxite, and deprived it, by careful heating, of various percentages of its combined water, and then extracted the alumina with 50° B. sulphuric acid at 100°.

The results are in Table III.

The sample contained 60 per cent. of alumina.

EFFECT OF CALCINING ON SOLUBILITY.

TABLE III.

					Soluble alumina. Per cent.
Dried at 100° C. not calcined	.....				59.00
Loss on calcining, 12.55 per cent	.....				57.60
“ “ 18.55 “ “	.....				57.10
“ “ 26.60 “ “	.....				53.10
“ “ 32.15 “ “	.....				20.40

Calcination certainly tends to decrease the solubility of the alumina, but does not constitute a serious menace until about 80 per cent. of the total combined water is removed. With a loss of about 38 per cent. of the water there is a loss of 1.40 per cent. soluble alumina; with a loss of about 58 per cent. of the combined water the loss of soluble alumina is 1.9 per cent. ; with a loss of about 82 per cent. of the combined water there is a much greater loss of soluble alumina; viz., 5.9 per cent. while the loss of soluble alumina rises to 38.60 per cent., when the material is thoroughly calcined. These results would seem to indicate that the material could be calcined until something more than half of its combined water was removed, without seriously affecting the solubility of the alumina, but the practical difficulties in the way of maintaining a uniform calcination at this point would certainly have to be considered. Unless the saving in freight would

more than counterbalance the loss in soluble alumina, there would appear to be no good reason for calcining. The percentage of available alumina (*i. e.*, the alumina dissolved by carrying the treatment with acid to fumes of so-called sulphur trioxide) is decreased by thoroughly calcining the bauxite, but the loss is not serious. In one experiment the 'available' alumina in the sample, dried at  $100^{\circ}$  C., was 57.20 per cent. and in the thoroughly calcined material 56.40 per cent.; in another sample 55.30 per cent. and 54.54 per cent. In one sample the loss was more considerable, the percentages being 54.87 per cent. and 49.50 per cent.

On the whole we can not recommend that the analytical sample be calcined previous to treatment with acid, whether by the old or the proposed new method, as a serious loss of dissolved alumina *may* be the result.

#### ANALYTICAL METHOD RECOMMENDED.

The analytical sample is to be passed through a sieve of 100 meshes per linear inch.

*Moisture*.—Two grams to constant weight at  $100^{\circ}$  C.

*Available Alumina*.—Two grams bauxite, ten cc. cold sulphuric acid of  $50^{\circ}$  B.

Heat gradually in a casserole until fumes of the so-called sulphuric anhydride appear, stirring the while to break up any small pieces; cover with a watch-glass and heat for ten minutes. Cool, add 100 cc. hot water, and boil for five minutes. Filter, and wash free of acid and alum with hot water. Cool filtrate, make up to 200 cc., and take out fifty cc. (equal to five-tenths gram) for alumina, ferric oxide, and titanium dioxide, and fifty cc. for titanium dioxide and ferric oxide,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ .

*Estimation of Available Alumina*.—The fifty cc. (equal to five-tenths gram) is diluted to 300 cc., two cc. hydrochloric acid added, heated to boiling, and ammonia added slowly to slight excess. The contents of the beaker are kept boiling for five minutes, filtered hot, and thoroughly washed with hot water. The precipitate is dried, ignited, and weighed as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ . The  $\text{Al}_2\text{O}_3$  is given by subtracting the  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  obtained in other operations.

*Estimation of Titanium Dioxide.*—Fifty cc. (equal to five-tenths gram) of the main solution are carefully neutralized with ammonia, the ammonia being added until there is a slight permanent precipitate. This precipitate is dissolved in sulphuric acid, added carefully so that there shall be but a slight excess; the volume is then made up to 350 to 400 cc. and boiled for one hour. If much iron is present, shown by the color of the main solution, it is best to deoxidize with sulphur dioxide, led into the boiling solution in which the titanium dioxide is being precipitated, but if there is only a small amount of iron present sulphurous acid may be used. In either case, however, it is well to maintain the volume of the boiling solution at about the same point, by addition of fresh portions of water, and to be sure that it smells of sulphur dioxide during the boiling. By observing these precautions the titanium dioxide is completely precipitated practically free of iron. Filter hot, through double filters, and wash thoroughly with hot water, dry, ignite, and weigh as titanium dioxide.

*Estimation of Ferric Oxide.*—This is best determined in the filtrate from titanium dioxide, by reduction with zinc and titration with permanganate.

The weight of  $\text{TiO}_2 + \text{Fe}_2\text{O}_3$  subtracted from the weight of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  gives the  $\text{Al}_2\text{O}_3$ , and this is the "available alumina."

*Estimation of "Free Alumina."*—Two grams bauxite, ten cc. 50° B. sulphuric acid, in a four-ounce Erlenmeyer flask, provided with a perforated stopper. Heat for one hour in a water-bath at a temperature of 95° to 100° C. with frequent shaking. Add 100 cc. hot water and keep in bath for ten minutes. Filter, wash thoroughly with hot water, and for the estimation of alumina proceed as before, with this difference, however, that the titanium dioxide does not have to be determined, since none of it goes into solution. In the solution we have merely the free alumina, and a small amount of ferric oxide, which can be estimated in the usual manner and its weight subtracted from the weight of the  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ .

*Combined Alumina.*—The difference between the available alumina and the free alumina is the combined alumina.

We do not at this time wish to give an opinion as to the form in which this alumina exists. It may be as clay, as a lower hydrate, or a mixture of these and other alumina compounds. We have thus far disregarded the insoluble residue, whether from the acid carried to fumes, or from the treatment at  $100^{\circ}$  C.

In case it is desired to determine the total alumina, the total titanic acid, the total ferric oxide, and the silica, the insoluble residue from the treatment to fumes may be folded up in the paper, and ignited. When the paper is consumed, fuse the residue with potassium bisulphate, and allow to stand in cold water containing at least five per cent. of strong sulphuric acid several hours, or until completely decomposed. Filter off the silica, which should be perfectly white, wash thoroughly with cold water, and ignite the silica. In the filtrate the alumina, titanium dioxide and ferric oxide are determined as in the filtrate containing the available alumina. Adding these several amounts to those found in the estimation of the available alumina gives, of course, the totals.

We can not advise the determination of silica in the insoluble residue by treatment with hydrofluoric acid and sulphuric acid, as we have found that some of the titanium dioxide is also volatilized, and the loss is  $\text{SiO}_2 + \text{TiO}_2$ .

So far as we are aware Riley was the first to point out the volatilization of titanium dioxide as fluoride. It may be that some if not all of what is volatilized goes off as hydrogen titanofluoride, as Roscoe and Schorlemmer<sup>1</sup> state, that when titanium dioxide is dissolved in hydrofluoric acid, a sirupy liquid is obtained which is probably hydrogen titanofluoride,  $\text{H}_2\text{TiF}_6$ . Crookes,<sup>2</sup> in speaking of the estimation of titanium dioxide in silicious residues, says that on treating them with hydrofluoric acid "a titanium fluoride is formed at the same time, which can not be heated without the larger portion going off.". He quotes an experiment of Riley's in which 2.235 grams of titanium dioxide were dissolved in hydrofluoric acid, evaporated and ignited, and the residue weighed only 0.99 gram, a loss of 1.245 grams or 55.70 per cent. of the original weight.

By seven successive treatments of titanium dioxide with

<sup>1</sup> Treatise on Chemistry, 2, [II], 262.

<sup>2</sup> Select Methods in Chemical Analysis, Second Edition, p. 193.

hydrofluoric acid we found the following losses on 0.0700 gram ;  
*viz.*:

	Per cent.
0.0025	3.57
0.0240	34.28
0.0135	19.29
0.0058	8.29
0.0032	4.57
0.0015	2.14
0.0001	0.14
<hr/>	<hr/>
0.0506	72.28

While there is a gain in time by treating the insoluble residue with hydrofluoric acid and sulphuric acid and taking the loss as silica, and while the error introduced is, perhaps, of no consequence commercially, yet the fusion with potassium bisulphate is to be preferred. But unless the silica, and the total alumina, titanium dioxide and iron are required, it is not necessary to make a fusion, the data obtained by the two separate treatments with acid being, in most cases, entirely sufficient for the valuation of bauxite.

So far as our observation goes, and we analyzed many different kinds of bauxite, titanium dioxide is always present, and in some bauxites may rise to four per cent. The clay immediately next to the bauxite may contain one per cent. of titanium dioxide, as we have found eight-tenths per cent. In other clays associated with bauxite we have found mere traces, and in the nearby soils it rarely exceeds five-tenths per cent. The concentration of the titanium dioxide in the bauxite is a very interesting phenomenon, and worthy of more extended investigation.

The titanium dioxide in bauxite is partly soluble in sulphuric acid brought to fumes. By using the Pittsburgh method in bauxite acid analysis, or sulphuric acid alone to fumes, varying amounts of titanium dioxide are dissolved, as the following results show :

Total titanium dioxide.	Soluble titanium dioxide.	Per cent. soluble.
4.00	3.30	82.50
3.00	2.60	93.33
4.00	2.50	62.50

The percentage of soluble titanium dioxide, calculated on the total amount present, may fall as low as fifty per cent., but for the

most part appears to be about seventy-five per cent. No titanium dioxide seems to be dissolved by the acid at  $100^{\circ}$  C. during one hour, but as the temperature rises the solubility increases, and when brought to fumes considerably more than half is dissolved. The variations in the amount dissolved may be due to variations of the form in which the titanium dioxide is present, but on this point we have no definite information. In summing up the chief points in this paper, we desire to call attention to the following :

1. The importance of discriminating in the analysis of bauxite between the trihydrate of alumina, easily soluble in sulphuric acid, and the other compounds of alumina, difficultly soluble.

2. A change in the basis of valuation, by which the trihydrate of alumina is to be given a higher value than the alumina present in some other form.

3. The adoption of a new nomenclature, calling the alumina soluble in  $50^{\circ}$  B. sulphuric acid at  $100^{\circ}$  C. during one hour "free alumina," and that soluble in sulphuric acid to fumes "available alumina," the difference between them to be known as "combined alumina."

4. The adoption of a standard method of analysis binding alike on the producer, the broker, and the consumer of bauxite for alum-making.

THE PHILLIPS TESTING LABORATORY,  
BIRMINGHAM, ALA.

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## UPON THE SALTS OF HYDRONITRIC ACID.

By L. M. DENNIS AND C. H. BENEDICT, with Crystallographic Notes by A. C. GILL.

Received January 20, 1898.

IN the year 1890 Th. Curtius announced<sup>1</sup> his successful preparation of hydronic acid ( $\text{HN}_3$ ), and briefly described the trinitrides of barium ( $\text{BaN}_3$ ), silver ( $\text{AgN}_3$ ), and mercury ( $\text{Hg}_2\text{N}_3$ ). He mentioned also the existence of trinitrides of copper, iron, sodium, and ammonium. Since that time no further work upon the inorganic compounds of this most interesting acid was published until last year when thallic trinitride ( $\text{TlN}_3$ ) and thallic thallic trinitride ( $\text{TlN}_3 \cdot \text{TlN}_3$ ) were added to the list.<sup>2</sup> Having a large amount of the acid on hand, we have entered upon the systematic study of the compounds of hydronic-

<sup>1</sup> *Ber. d. chem. Ges.*, 23, 3023.

<sup>2</sup> Dennis and Doan : this Journal, 18, 970.

tric acid, and in this paper are given the results obtained with the elements in the principal group of Group I and the alkaline earths of Group II.

#### GROUP I.

*Lithium Trinitride*,  $\text{LiN}_3 \cdot \text{H}_2\text{O}$ .—This was made by neutralizing lithium hydroxide with hydronitric acid and allowing the solution to evaporate in the air. It separated in the form of colorless, glistening needles. It is very soluble in water and is hygroscopic. It is also soluble in alcohol. On being gently heated, the crystals lose their luster and water of crystallization is driven off. On further heating the salt breaks down, the decomposition being somewhat more violent than with the other compounds in this group. Upon standing, the lithium trinitride loses some hydronitric acid.

The hydronitric acid was determined by dissolving the salt in water, precipitating with silver nitrate, and converting the silver trinitride into silver chloride.<sup>1</sup> To the filtrate and washings from the first precipitation hydrochloric acid was added to precipitate the excess of silver, the silver chloride was filtered off, and the filtrate and washings were evaporated to dryness with sulphuric acid. The lithium was then weighed as the anhydrous sulphate. Analysis gave as follows :

	Calculated for $\text{LiN}_3 \cdot \text{H}_2\text{O}$ .	Found.
Lithium .....	62.72	63.03
Nitrogen .....	10.46	10.17
Water .....	26.82	(Diff.) 26.90

*Sodium Trinitride*,  $\text{NaN}_3$ .—This salt is mentioned by Curtius but he gives no analysis. It was prepared by the same method as that used for lithium, and upon evaporation of the solution it separates in clear colorless crystals. A freshly prepared aqueous solution of the crystals is neutral in reaction, but, upon standing, it becomes alkaline. The salt does not decompose easily when heated, but on the contrary may be melted and kept in a state of fusion for some hours without breaking down.

The analysis, which was made as described under lithium, gave as follows :

<sup>1</sup> Dennis : This Journal, 18, 950.



	Calculated for $\text{NaN}_3$ .	Found.
Sodium.....	35.38	35.42
Nitrogen .....	64.62	64.71

*Potassium Trinitride*,  $\text{KN}_3$ .—This compound, like all of the other trinitrides in this group, was made by neutralizing the hydroxide with hydronitric acid. On attempting to concentrate this solution on the water-bath, it became strongly alkaline. This loss of hydronitric acid was determined in one case by neutralizing a solution of potassium hydroxide with a known amount of the acid, evaporating to dryness on the water-bath and determining the acid in the residue. It was found that about four per cent. of the acid had passed off during the evaporation. To obtain crystals of the potassium salt the solution was allowed to evaporate spontaneously in the air and was kept very slightly acid by adding a drop or two of hydronitric acid every day. The salt crystallizes well and the crystals are stable in the air. They melt when heated and decompose only at a high temperature. Potassium trinitride is but slightly soluble in alcohol and is precipitated from aqueous solution by the addition of an excess of alcohol. Analysis gave

	Calculated for $\text{KN}_3$ .	Found.
Potassium .....	48.21	47.92
Nitrogen .....	51.79	51.72

*Rubidium Trinitride*,  $\text{RbN}_3$ .—This salt crystallizes in the form of fine needles. It is extremely soluble in water but is less soluble in alcohol than the potassium salt and, like it, can be thrown out of solution by the addition of alcohol. It fuses when gently heated and at a high temperature it decomposes with a puff and a flash. Analysis gave

	Calculated for $\text{RbN}_3$ .	Found.
Rubidium .....	32.99	32.58
Nitrogen .....	67.01	67.01

*Cesium Trinitride*,  $\text{CsN}_3$ .—On evaporating the solution of this salt it was found to lose hydronitric acid in spite of the strongly basic nature of the cesium. The trinitride was so very soluble in water that crystallization was brought about only by placing it over sulphuric acid. The crystals appeared as clear, colorless

needles, gathered together in fern-like clusters. The salt is almost completely insoluble in alcohol. The crystals decompose only when highly heated. Analysis gave

	Calculated for $\text{CsN}_3$ .	Pound.
Cesium .....	75.99	76.03
Nitrogen .....	24.01	24.36

All of these trinitrides of the alkalis are quite stable in the air, the lithium salt being the only one that tends to lose a part of its acid on exposure. None of the salts are what we should term explosive and the ease of decomposition by heat decreases as the atomic mass of the base rises. In solubility they resemble the chlorides of the alkalis, all of them being soluble in water and the solubility increasing with the atomic mass of the base. The solubility in alcohol is the reverse of that in water, lithium trinitride being quite soluble in alcohol and cesium trinitride being insoluble.

#### THE ALKALINE EARTHS.

*Calcium Trinitride*,  $\text{CaN}_3$ .—This was prepared by dissolving calcium oxide in a dilute solution of the acid and crystallizing over sulphuric acid, the solution decomposing if evaporated on the water-bath. The crystals separate as small, white hemispherical aggregations which under the microscope are seen to be made up of very small crystals of unrecognizable form. The salt explodes with considerable violence when heated. In analyzing the trinitrides of the alkaline earths, the hydronitric acid was determined in one portion by the method above described, and another portion was treated with sulphuric acid and the base weighed as the sulphate. The results for the calcium salt were

	Calculated for $\text{CaN}_3$ .	Pound.
Calcium .....	67.74	67.63
Nitrogen .....	32.26	31.97

*Strontium Trinitride*,  $\text{SrN}_3$ .—This was prepared by dissolving strontium oxide in a two per cent. solution of hydronitric acid, and crystallizing over sulphuric acid. The crystals separate in the same peculiar hemispherical form as does the calcium trinitride. The strontium trinitride is more soluble in water than is the cal-

cium salt, and is less soluble than the barium trinitride. Analysis gave

	Calculated for SrN <sub>6</sub> .	Found.
Strontium.....	51.05	51.21
Nitrogen .....	48.95	48.71

*Barium Trinitride*, BaN<sub>6</sub>.H<sub>2</sub>O.—Curtius has described<sup>1</sup> the anhydrous barium trinitride. Although we used the same method of preparation, the crystals contained water, as could be seen by gently heating the salt in a glass tube, and as is indicated by the analysis :

	Calculated for BaN <sub>6</sub> .H <sub>2</sub> O.	Found.
Barium.....	57.32	57.10
Nitrogen .....	35.14	35.01
Water .....	7.54	(Diff.) 7.89

The salt crystallizes in glistening needles which lose luster on standing. They explode with quite a loud report when heated, the particles shooting about like miniature rockets.

The trinitrides of this group are soluble in water, the solubility increasing with the rise in the atomic mass of the base. All of them explode when heated, the violence of the explosion diminishing as the strength of the base increases. They become basic when exposed to the air. The solutions of the trinitrides in water also slowly lose some hydronitric acid upon standing, and quickly become basic when heated upon the water-bath.

#### CRYSTALLOGRAPHIC NOTES BY A. C. GILL.

The following crystallographic notes on the salts of the acid HN<sub>3</sub> with the bases Li, Na, K, Rb, Cs, Ca, Sr, and Ba were made from a study of material furnished by Mr. C. H. Benedict of the Chemical Department of Cornell University.

Since the lithium and barium compounds crystallize with a molecule of water each, they are not strictly comparable with the others, though the fact in itself proves, of course, a certain difference in their character. The series of anhydrous alkali salts presents the not uncommon phenomenon that the sodium compound behaves differently in its crystallization from the corresponding compounds of K, Rb, and Cs. The latter three are

<sup>1</sup> *Loc. cit.*, p. 3032.

strictly isomorphous, as might have been predicted *a priori*. In the case of the alkaline earths, however, the unusual condition obtains that calcium acts more like strontium than does barium. The detailed observations made on the material in hand are as follows :

$\text{LiN}_3 \cdot \text{H}_2\text{O}$ , *hexagonal* (?).—The fine colorless needles, one to three mm. in length, deliquesce on exposure to the air so that no measurements were obtained on the goniometer. The cross-section of these needles, as seen by setting them on end in wax under a microscope with low power objective, seems to be hexagonal or triangular, though the rapid deliquescence entirely rounds off the angles almost before an observation can be made. The crystals have parallel extinction with greatest optical elasticity in the direction of elongation. They are, thus, probably hexagonal and optically negative. The double refraction is very strong,—about 0.250 as determined by interference colors under crossed nicols.

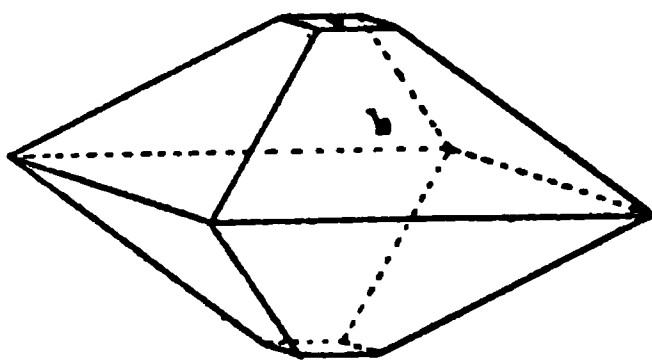
$\text{NaN}_3$ , *hexagonal*.—Crystals of this substance exhibit a very varied habitus, but only the extremely thin basal plates, among the crystals studied, furnished any crystallographic data. These show irregular outlines, and have a diameter of one to two and one-half mm., with a thickness of 0.02 to 0.1 mm. Lines of cleavage making an angle of  $60^\circ$  (rarely  $30^\circ$ ) are plainly visible in many places. In converged polarized light the optical interference figure is uniaxial and positive. The hexagonal form is thus established beyond question. The strength of the double refraction of this substance is remarkable, for a 0.1 mm. plate shows the colored rings of its interference figure much closer together than in a calcite plate two and one-half times as thick.

$\text{KN}_3$ , *tetragonal*.—Brilliant colorless transparent crystals from two to five mm. in diameter gave excellent measurements on the goniometer. The shape of these is seen in the figure where  $p$  = the base, (001), and  $b$  = the pyramid (111). The axial ratio  $a : c = 1 : 0.57976$ . This is computed from twenty-one measurements of the angle 111 to  $\bar{1}\bar{1}\bar{1}$  which varied from  $78^\circ 40'$  to  $78^\circ 44'$ , averaging  $78^\circ 41' 45''$ . The calculated polar angle 111 to  $\bar{1}\bar{1}\bar{1}$  is  $53^\circ 16' 34''$ ; found,  $53^\circ 16' 15''$ . The base is too rough to give good reflections, but is always present. The prism (110), on the other hand, is very rarely to be seen, but

in one case gave a sharp image in the telescope of the goniometer. The crystals are optically uniaxial, negative, and very strongly doubly-refracting:

$\text{RbN}_3$ , *tetragonal*.—In general appearance these crystals differ from those of  $\text{KN}_3$ , only in having the basal plane more largely developed, so that their habitus is tabular rather than pyramidal. The angle from base (001) to pyramid (111) is about  $40^\circ 13'$  (average of eleven measurements varying from  $39^\circ 51'$  to  $40^\circ 35'$ ) whence  $a : c = 1 : 0.5979$ . The double refraction is negative, like that of  $\text{KN}_3$ , but decidedly weaker.

$\text{CsN}_3$ , *tetragonal*.—No good crystals for goniometric measurement were at hand, but under the microscope they showed themselves similar in shape to the preceding. They are uniaxial, negative, and weaker in double refraction than  $\text{RbN}_3$ . Under crossed nicols the interference colors of crystal fragments indicate a double refraction of 0.050. The basal plates are often



traversed by twin lamellae. One specimen having a sharp rectangular outline showed these lamellae at angles of  $90^\circ$  with each other, but turned  $10^\circ$  with reference to the outline of the crystal. Hence this substance, and probably the two foregoing, is very likely pyramidal hemihedral.

$\text{CaN}_3$ , *orthorhombic* (?).—This substance was seen only in the shape of milk-white balls or spherules composed of radiating needles. On crushing, these showed under the microscope parallel extinction, with the greater elasticity in all cases in the direction of elongation of the needle. Since the double refraction appears to vary from 0.070 to 0.100, the substance is probably orthorhombic, rather than tetragonal or hexagonal.

$\text{SrN}_3$ , *orthorhombic*, (?).—It resembles very closely the foregoing, and could be investigated only to the same limited extent. The double refraction is slightly stronger, and the spherulitic aggregates are less perfectly round than is the case with  $\text{CaN}_3$ .

$\text{BaN}_2 + \text{H}_2\text{O}$ , *triclinic*.—The brilliant little crystals of the barium salt have a six-sided prismatic habitus, with terminating faces usually at only one end. The other end is frequently attached to another individual in twinning position, the long axes of the two making an angle of about  $65^\circ$ . The small size and irregular surface of the crystals prevented measurements of sufficient accuracy to determine the axial ratios. The angle which would be naturally chosen as that of the prism measures  $66^\circ 12'$ . Since the extinction angle is  $22^\circ$  when the obtuse interior angles of this prism are placed in a vertical plane one above the other, and  $10\frac{1}{2}^\circ$  when the crystal is turned  $90^\circ$  about its long axis, the crystal system must be triclinic. The double refraction is extremely high, above 0.200, and the mean index of refraction is about 1.7.

CORNELL UNIVERSITY,  
JANUARY, 1898.

## INTRODUCTORY NOTE ON THE REDUCTION OF METALLIC OXIDES, AT HIGH TEMPERATURES.

By FANNY R. M. HITCHCOCK.

Received January 22, 1898.

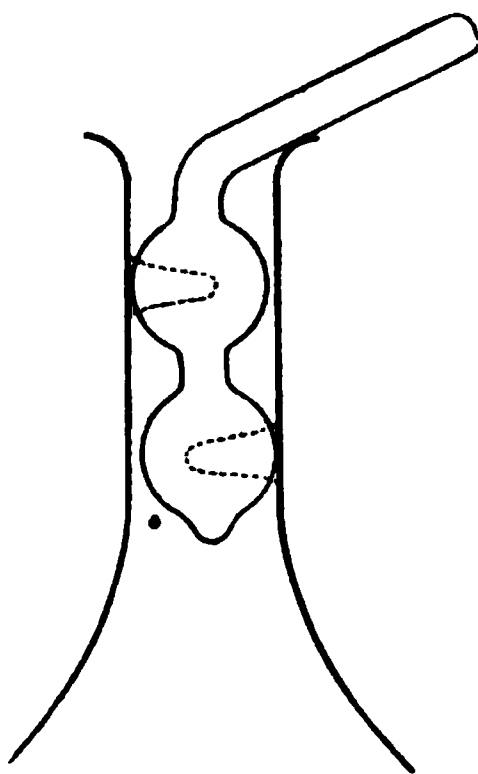
A consideration of the results obtained by Dr. Friedheim and the author, when working on the atomic mass of tungsten in 1895, and 1896, led me to the conclusion that the loss in weight of the metallic oxides on reduction in hydrogen was not due solely to oxygen. Experiments made at high temperatures showed nitrogen was given off steadily though very slowly from tungstic oxide and from molybdic oxide, when reduced in a current of hydrogen. On decreasing the temperature the amount of nitrogen decreased; on raising the temperature again, nitrogen was given off in greater quantities. While the spectrum of the gas gave only the appearance of nitrogen, and no trace of argon or helium could be found on sparking with oxygen, yet the densities were abnormal, and indicated the presence of gases both lighter and heavier than nitrogen. The nitrogen obtained on reduction in porcelain tubes at the temperature obtainable with a Glaser furnace gave densities varying from two to eight ( $H = 1$ ). The gas obtained when a Lorenz furnace was used gave densities of from twenty-two to twenty-six.

In this latter gas argon may be present. The results obtained by an examination of the gas from different metallic oxides indicate that nitrogen is generally present in greater or less amounts; and the low results for atomic weights obtained by the reduction method might be thus easily accounted for. Ferric oxide, prepared from ferrous oxalate, which was made from pianoforte wire, showed a noticeable amount of nitrogen. The results obtained with other oxides will soon be ready to communicate; as the experiments are not completed and the examination of the gases is still under way, the author desires for the present to reserve this field of research.

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### NOTES.

*Device to Prevent Loss from Spattering.*—To prevent loss from spattering or bumping when boiling liquids in flasks, the writer



has devised the arrangement herein described, and found it to work very satisfactorily,—much more so than a watch-glass cover. The accompanying diagram is almost self-explanatory. Two bulbs are blown on the end of a piece of glass tubing which is then bent and finished as shown. The bulbs should fit quite loosely in the neck of the flask and the exterior handle should incline downward into the flask so as to return anything condensed thereon. It will be found that the escaping vapors will condense on the bulbs and form liquid joints at the points indicated by the dotted lines. As these joints are always on opposite sides of their respective bulbs, they form a complete obstruc-

tion to spattering liquids but allow gases to freely escape through the circuitous course around them.

The arrangement is especially useful in making copper assays where the sulphuric acid used in expelling the other acids frequently humps badly. A single bulb, hanging well down in the neck of the flask, is often quite sufficient but two bulbs are better.

ALBERT H. LOW.

LABORATORY OF VON SCHULZ & LOW,  
DENVER, COLO., JANUARY 20, 1898.

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### CORRESPONDENCE.

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WASHINGTON, D. C., February 14, 1898.

*Editor Journal of the American Chemical Society:*

*Dear Sir.*—The Organization Committee of the Third International Congress of Applied Chemistry, which is to be held in Vienna during the coming summer, has fixed the date of the meeting from July 28, to August 2, 1898. Some time during the month of February, programs and announcements will be sent to all persons who have been enrolled as members of the Congress.

Respectfully,

H. W. WILEY,

Chairman of the American Committee.

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WASHINGTON, D. C., February 23, 1898.

*Editor Journal of the American Chemical Society:*

*Dear Sir.*—The committee appointed by the president of the society, in harmony with the resolution of the board of directors adopted at the meeting of October 7, 1897, has considered the question of a want column in the Journal. We propose that such a column be opened in the Journal for the use of the members of the society who may desire to secure employment, and for the use of employers who may desire to secure the professional services of members of the society.

We therefore wish to announce to members seeking employment or new fields of labor, that they are invited to insert a notice to that effect in the advertising columns of the Journal, free



of charge, the notice not to exceed the space of three one-half inch insertions. We also desire to inform employers, companies, and corporations desiring the professional services of members of the society, that they may insert an advertisement to that effect, of the space of three one-half inch insertions in the columns of the Journal free of charge. The advertisements should be sent to the editor of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Easton, Pa.

Respectfully,

H. W. WILEY,  
CHARLES E. MUNROE,  
F. W. CLARKE,

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### NEW BOOKS.

RESEARCHES ON THE MOLECULAR ASYMMETRY OF NATURAL ORGANIC PRODUCTS. BY LOUIS PASTEUR, membre de la Société Chimique de Paris, (1860). Alembic Club Reprints, No. 14. Edinburgh: William F. Clay. 1897. Cloth. 46 pp. Price, 1s. 6d.

In presenting this important paper in English translation the Alembic Club has rendered a valuable service to chemists interested in the history of the rise and development of fruitful scientific theories. The study of the phenomena of rotary polarization of organic substances has led to the discovery of most important peculiarities in the constitution of the complex compounds of carbon, and in this paper by Pasteur we find described in a simple yet masterly style the several steps which led him up to his first great generalization on the subject of optical isomerism. In the early 40's he became engaged in a study of the relation of the crystalline forms of certain tartrates to their observed optical rotations. In 1848 he was able to announce the isolation of the right- and left-handed tartaric acids from ammonium sodium racemate; this pioneer discovery was followed by others published at frequent intervals, all of which attracted much attention. In 1860 the Chemical Society of Paris invited Pasteur to deliver two lectures covering the matter of his investigations in this field. The lectures were given in semi-popular form and published in the following year. The Alembic Reprint is simply the translation of the lectures as given in 1860. The translator very properly calls attention to

the fact that later investigations have not modified the theories advanced by Pasteur in any essential particular, and further that they must be considered as paving the way for the able and fruitful hypotheses of LeBel and van't Hoff on the relations of asymmetric carbon atoms, published many years later.

J. H. LONG.

A HANDBOOK FOR CHEMISTS OF BEET-SUGAR HOUSES AND SEED-CULTURE FARMS. BY GUILFORD L. SPENCER, D. Sc., of the U. S. Department of Agriculture. First Edition. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. 1897. x + 475 pp. Price, \$3.00.

This work is the outcome of the favorable reception accorded the author's Handbook for Sugar Manufacturers, and of the increased importance of beet-sugar manufacture in the United States.

In it are given short and easily understood directions for sampling and analyzing the raw material and products which the chemist of a beet-sugar house or seed-control farm has to deal with; many hints on sugar-house work and chemical control; and a very complete set of tables; all combining to make a handbook which cannot but be of service to the man of wide, as well as the man of limited experience. It is to be regretted that so many sugar-house managers think it economy to employ as chemists, men with a very limited knowledge of chemical theory and manipulation, but such is the case, and this handbook contains much that will prevent such men from going astray, as well as much to encourage further study.

I can endorse the author's statement that many so-called "undetermined losses" are due to errors in measuring, sampling, or methods of analysis. Throughout the book the author gives evidence of an appreciation of the difficulties in effecting chemical control—difficulties which the merely theoretical man is apt to overlook or underestimate.

EDMUND C. SHOREY.

A PRACTICAL TREATISE ON MINERAL OILS AND THEIR BY-PRODUCTS, INCLUDING A SHORT HISTORY OF THE SCOTCH SHALE OIL INDUSTRY, ETC. BY ILTYD I. REDWOOD. London: Spon; New York: Spon & Chamberlain. 8vo. 336 pp., with 67 illustrations. Price, \$6.00.

The work opens with an interesting chapter upon the history of the subject, which is followed by a geographical and geolog-

ical description of the occurrence of shale. The theory of the process of manufacture is then discussed: it is shown that the oil does not exist in the shale as such but is formed by destructive distillation. This gives rise to oily bases and phenols which have to be removed. The refining of shale oil is therefore a much more difficult and delicate process than that of petroleum.

The main part of the book is taken up with the practical treatment: the operations of distilling, refining, treating, and pressing are minutely described and discussed, the size of the apparatus, the yield, and the costs being given. The by-products and recovered products, ammonia, soda, acid, and waste water, are next detailed.

The last chapter deals with the tests applied in the process, from time to time, and the laboratory method of testing wax, oil, and ammonia. The work closes with an appendix giving an abstract of all the patents which have been obtained in connection with this industry.

A. H. GILL.

A SHORT HANDBOOK OF OIL ANALYSIS. BY AUGUSTUS H. GILL, S.B., PH.D. Philadelphia: J. B. Lippincott Co. 1898. Cloth. 139 pp. Price, \$1.50.

This little volume is evidently written with the idea of furnishing students with brief outlines of the best methods of oil analysis known at the present time, and also short descriptions of the oils in common use, their properties and the sources from which they are derived.

As an introduction to the study of oils, and for practical use in the laboratory, it will be found an admirable text-book, while the copious reference notes will enable the student to readily follow the subject further, if he so desires.

Part I is devoted to the physical and chemical tests used to identify the various oils, determine their purity, and ascertain their fitness for a given purpose. Petroleum products are first discussed, one chapter being devoted to burning oils and the tests commonly applied to them, and another to lubricating oils. Then follows a chapter on animal and vegetable oils, and the tests used to identify them, determine their purity, and detect adulterants.

The author has rightly emphasized the desirability of having

samples of undoubted purity with which to compare the oil under process of identification, as even the so-called "constants" are so variable in the case of oils, that one may be easily misled, especially where only a small amount of an adulterant is present. On the general subject of lubrication the author is a little too brief to leave a clear impression in the mind of the student.

The rank which is given mineral oils as having greater adhesion and less cohesion than animal and vegetable oils is open to question, for while this may be true at ordinary temperatures, it will not be found the case when the parts requiring lubrication become warm from any cause, and the lubricant is most needed. At high temperatures nothing but the most viscous fat oil we can obtain will adhere to the heated surfaces, and it is for this reason that a percentage of an animal or vegetable oil is added to cylinder oils—in order to give the adhesiveness which is wanting in petroleum products at cylinder temperatures. This emphasizes the desirability of determining the viscosity of an oil at the temperature at which it is to be used.

Part II contains brief descriptions of the various oils in common use, giving their source, preparation, constants, adulterants, and uses, in a concise and comprehensive manner.

The appendix contains much valuable information in tabulated form.

O. S. DOOLITTLE.

AN INTRODUCTORY COURSE IN QUANTITATIVE ANALYSIS. BY PERCY W. EVANS, PH.D., Associate Professor of Chemistry, Purdue University. Boston: Ginn & Co. 1897. iv + 83 pp. Price, 55 cents.

The little book of Prof. Evans offers within a scope of eighty pages a very instructive course in quantitative analysis, including gravimetric and volumetric methods, together with a discussion of the various manipulations with which every student of this branch should become familiar as a preliminary. The exercises are well chosen and the explanations clear and comprehensive. As a handbook it might well find use in many college laboratories.

F. C. PHILLIPS.

EXERCISES IN PRACTICAL PHYSIOLOGY. PART III. PHYSIOLOGY OF THE NERVOUS SYSTEM. ELECTRO-PHYSIOLOGY. By Augustus D. Waller, M.D., F.R.S. London, New York, and Bombay: Longmans, Green & Co. 91 pp. Price, 90 cents.

As the title indicates, this is a practical or laboratory hand-

book and is intended to accompany the third edition of the author's well-known "Introduction to Human Physiology." In ninety-one pages of matter the student, who is supposed to have had a year's training in general physiology, is given careful directions for performing a large number of important experiments relating to the physiology of the nervous system. The book makes no pretense to being anything more than a laboratory guide, and from this standpoint the selection of exercises it presents must be considered excellent and well chosen. Most of the experiments are adapted to the needs and understanding of that growing class of students in our medical schools which demands thorough training in physiology and chemistry as preliminary to a proper appreciation of clinical demonstrations, and to such students the book can be recommended.

J. H. LONG.

THE CHLORINATION PROCESS. BY E. B. WILSON, E.M. New York: John Wiley & Sons. 1897. 12 mo. cloth. v + 125 pp. Price, \$1.50.

This book was evidently written to meet the present demand for information regarding gold. It is mild to say that the work was poorly done. It is mainly an undigested mass of citations tied up with confused and misleading statements which injure the utility of even the best quotations.

The author's statements are often inexact and frequently contrary to fact. For instance, he uses "chlorine" as synonymous with "chloride" and "chlorination" with "chloridizing roasting." Also, page 23, he makes this astounding statement: "Copper sulphides can be readily freed from their sulphur by slow roasting at a moderate heat, with or without salt." And, page 87, he gives the reaction on bringing hydrogen sulphide gas into acid auric chloride solution as  $2\text{AuCl}_3 + \text{H}_2\text{S} + 2\text{H}_2\text{O} = 2\text{Au} + 6\text{HCl} + \text{SO}_2$ .

One looks in vain for any critical discussion of the chlorination process and its particular field of application, or for any tests to determine whether a given ore would be suitable for this process. In fact, Dr. Godshall's article in the *Engineering and Mining Journal*, Jan. 6 and 13, 1894, is a far better guide in investigating the chlorination process than Wilson's book.

FREDERIC P. DEWEY.

**ORGANIC CHEMISTRY FOR THE LABORATORY.** BY W. A. NOYES, PH.D.  
Illustrated. xii + 257 pp. Easton, Pa.: The Chemical Publishing Co.  
Price, \$1.50.

Several excellent works on the preparation of organic compounds have recently appeared and it can no longer be said that the absence of comprehensive guides of this kind is a cause for complaint. Some of these have been kindly received by the critics and now this latest addition seems to be wholly worthy of equal praise. After an examination of this volume one feels that it may without apology be placed beside the best of similar efforts, although it is not intended to occupy precisely the same field as other laboratory guides.

Professor Noyes has done this work in a systematic form and evidently with great care; he has made it comprehensive enough to include the best methods of preparing the principal classes of carbon compounds, not confining himself to single examples in any class. The result is a reference book which can be used by the student but which also presents much more than the average student will attempt to accomplish. It does not outline a course of study nor are the various preparations presented in the order which a student would be likely to follow. The work is essentially for reference, adapted to the needs of advanced workers and instructors, although no part is beyond the capacity of the ordinary student who may wish to select certain of its contents for his own use.

There are twelve chapters, dealing in the order named, with acids; acid derivatives; halogen compounds; nitro compounds; amines; hydrazo, azo, and diazo compounds; alcohols and phenols; aldehydes and ketones with their derivatives; sulphonic acids; hydrocarbons; miscellaneous compounds; and qualitative reactions and reagents.

The method of treatment of these subjects follows a uniform order. Each chapter opens with a general discussion of the principal methods relating to the group of compounds under consideration, and then follows the discussion, in detail, of typical compounds within the group. Under acids, nineteen distinct examples are fully discussed and other groups are treated with appropriate fulness. Each preparation is described systematically, beginning with a statement as to the general character of

the method, and the specific character of the preparation to be undertaken. Then comes a summary of the literature bearing upon the subject ; an exact statement of the kind and amounts of the materials required ; and finally a careful description of the operation to be performed. Graphic formulas are freely employed, and the author frequently takes occasion to point out some historical significance or some general application of the particular experiment under discussion. Cross references are numerous and the book is well indexed. In all, ninety-six separate preparations are fully described.

The mechanical work of the book has been well done, although the illustrations can hardly be called elegant. This criticism applies so frequently to scientific literature that it suggests the possibility of the employment of conventional designs for the representation of common forms of apparatus like flasks, burners, coolers, receivers, supports, washing and drying vessels, etc., which would admit of common use, would be inexpensive and would serve for illustration in a simple and understandable way. The book is not wholly free from typographical errors and an occasional "chemical idiom," but these detract in no way from the highly creditable character of the work, which will without doubt be well received and successfully realize the author's purpose.

W. E. STONE.

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### BOOKS RECEIVED.

**Laboratory Experiments on the Class Reactions and Identification of Organic Substances.** By Arthur A. Noyes, Associate Professor of Organic Chemistry in Massachusetts Institute of Technology, and Samuel P. Mulliken, Instructor in Organic Chemistry in Massachusetts Institute of Technology. Second, Thoroughly Revised Edition. Easton, Pa.: The Chemical Publishing Co. 28 pp. Price, 50 cents.

**The Freezing-point, Boiling-point, and Conductivity Methods.** By Harry C. Jones, Instructor in Physical Chemistry in Johns Hopkins University. Easton, Pa.: The Chemical Publishing Co. vii + 64 pp. Price, 75 cents.

**Twenty-first Annual Report of the Connecticut Agricultural Experiment Station for 1897.** Part II. Fertilizers. 93 pp. Part III. Mildew of lima beans ; Prevention of leaf-blight and leaf-spot of celery ; Cause and prevention of a fungus disease of the apple ; Investigations on a disease of carnations ; Literature of fungus disease. 64 pp. The Connecticut Agricultural Experiment Station, New Haven, Conn.

The Irish Potato. Bulletin No. 42. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas. 16 pp.

Nitrogenous Feeding Stuffs. By C. L. Phelps. Bulletin No. 18. December, 1897. Storrs Agricultural Experiment Station, Storrs, Conn. 16 pp.

Analysis of Commercial Fertilizers and Paris Green. Bulletin of the Agricultural Experiment Station. Second Series, No. 49. Louisiana State University and Agricultural and Mechanical College, Baton Rouge, La. 42 pp.

Observations on Recent Cases of Mushroom Poisoning in the District of Columbia, United States Department of Agriculture, Division of Botany, Washington, D. C. 24 pp.

The Proceedings of the Chemical and Metallurgical Society of South Africa. May, 1895-January, 1897. Vol. I. Edinburgh, R. W. Hunter : Johannesburg, S. A. R.: The Chemical and Metallurgical Society of South Africa, 12 Chamber of Mines Building. 348 pp.

Bibliography of the Metals of the Platinum Group—Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium—from 1748-1896. By Jas. Lewis Howe. City of Washington : Smithsonian Institution. 1897. 318 pp.

Tobacco Soils of the United States : A Preliminary Report upon the Soils of the Principal Tobacco Districts. By Milton Whitney. Bulletin No. 11. U. S. Department of Agriculture, Division of Soils. Washington, D. C. 1898. 47 pp. and 13 plates.

Das optische Drehungsvermögen organischer Substanzen und dessen praktische Anwendungen. Bearbeitet von Dr. H. Landolt, unter mitwirkung von Dr. Schönrock, Dr. P. Lindner, Dr. F. Schütt, Dr. L. Berndt, Dr. T. Posner. Zweite gänzlich umgearbeitete auflage, mit eingedruckten abbildungen. Braunschweig : Friedrich Viewig und Sohn. 1898. xxiv + 655 pp. Price M 18.

The Arrangement of Atoms in Space. By J. H. van't Hoff. Translated and edited by Arnold Eiloart. Second enlarged and revised edition. Longmans, Green & Co., London, New York, and Bombay. 1898. xi + 211 pp. Price \$1.75

On Laboratory Arts. By Richard Threlfall, M. A. New York : The Macmillan Co. 1898. xii + 338 pp. Price \$1.50.

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## ERRATUM.

In the last (February) issue of the Journal on page 101, line 10, for "damp mercury" read "damp air."



# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

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## THE MOIST COMBUSTION METHOD OF DETERMINING CARBON IN STEEL.

BY GEORGE AUCHY.

Received February 9, 1898.

SOME recent experiences of the writer with the wet method of combustion show that this process may sometimes work faultily in the following particulars: First, the potash bulbs may not absorb all the carbon dioxide; Second, the "prolong" containing calcium chloride may not absorb all the moisture drawn over from the potash bulb; Third, the proportion of moisture so escaping from the prolong is not uniform and unvarying; Fourth, the potash solution may lose something besides moisture; Fifth, some chloro-chromic compound other than that absorbed by Prof. Langley's "pyro" mixture may occasionally form and cause high results.

With regard to the first of these points, it is the almost universal custom to use for the absorption of the carbon dioxide, a single set of weighed potash bulbs as directed by Blair in his description of the wet method. Prof. Langley, however, uses solid potash after the bulbs. Others use soda-lime tubes instead of potash bulbs. The writer in making determinations using the potash bulbs as customary obtained results varying very widely and was very much puzzled by them, believing at that time one set of bulbs to be ample for the complete absorption of the carbon dioxide. It was finally found, however, that a single set of bulbs is not always sufficient to absorb all the carbon dioxide in the wet method of combustion. Following are

the varying results spoken of, using but one set of potash bulbs.

	Per cent.		Per cent.
Steel 59 (Fresh potash).....	1.97	Steel 1.00 standard .....	0.974
" 59 .....	2.13	" 1.00 " .....	0.870
" 59 .....	2.25	" 1.00 (Fresh potash) .	0.890
" 59 .....	2.07	" 35 .....	0.333
" 59 (Fresh potash).....	2.01	" 35 .....	0.288
" 59 .....	2.277	" 17 .....	0.636
" 59 (Fresh potash).....	2.18		

Two sets of potash bulbs were then employed with a calcium chloride prolong to each. After the second set of bulbs and prolong used, a weighed set of potash bulbs with the two anterior bulbs containing strong sulphuric acid was also used, the last bulb empty to avoid all danger of mechanical loss. Following this was the usual calcium chloride guard tube.

	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Steel 59.....	2.267	none	2.267
" 59.....	2.280	none	2.280
" 1.00 standard .....	0.88	0.124	1.004
" 1.00 " .....	1.005	none	1.005
" 35 .....	0.261	0.039	0.30
" 35 .....	0.239	0.073	0.312
" 17 .....	0.631	0.031	0.662
" 81 .....	2.257	0.155	2.412
" 81 .....	2.278	0.042	2.320 <sup>1</sup>
" 81 .....	2.115	0.285	2.400
" 80 .....	3.145	0.070	3.215
" Tool.....	1.009	none	1.009
" 60 .....	2.30	0.09	2.39
" a4 .....	0.841	0.041	0.882
" a5 .....	0.853	0.053	0.906
" a6 .....	0.823	0.026	0.849
" 2hh .....	1.014	0.051	1.065
" 92 .....	0.693	0.302	0.995
" 93 .....	1.033	0.151	1.184
" 94 .....	1.010	0.052	1.062
" 94 .....	0.896	0.176	1.072
" 95 .....	1.018	8.080	1.098
" 100 .....	0.206	0.064	0.27
" 101 .....	0.044	0.021	0.065
" 20 .....	2.54	0.70	3.24

<sup>1</sup> This result is too low on account of incomplete solution of the steel by the double chloride solution.

The following were obtained by combustion with lead chromate and potassium dichromate :

	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Steel 96.....	0.626	0.348	0.974
" 97.....	0.732	0.366	1.098

In all the above determinations the potash used was of specific gravity 1.27 as is customary and was frequently changed. In the following the strength of the potash solution was increased to 1.40 specific gravity. This latter strength was found much preferable, not only on account of the solution of that strength possessing greater absorbing power, but also because it can be used much longer in the potash bulbs without change :

Steel.	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Tool, large.....	1.146	0.005	1.151
Tool, small.....	1.128	0.032	1.16
Nov. 13.....	1.14	none	1.14
Slab.....	1.103	0.015	1.118
E.....	1.042	none	1.042
T.....	1.023	none	1.023
Slab.....	1.09	0.02	1.11
106.....	1.379	none	1.379
No. 7.....	1.06	none	1.06
Cross cut.....	1.007	none	1.007
106.....	1.372	none	1.372
20.....	3.499	0.020	3.519
III R.....	0.858	none	0.858
II0.....	1.136	0.010	1.146
II3.....	1.134	none	1.134
II4.....	1.251	0.019	1.27
II5.....	1.104	0.016	1.12
II5.....	1.091	0.050	1.141
II6.....	0.986	0.036	1.012
II8.....	1.02	0.012	1.032
II9.....	0.925	0.031	0.951
Trial.....	2.171	0.273	2.444
120.....	0.719	0.064	0.783

*With fresh potash (sp. gr. 1.40).*

123.....	0.771	0.006	0.777
121.....	0.635	0.010	0.646
122.....	0.279	0.001	0.28
Shear.....	2.547	0.012	2.559

With new potash (sp. gr. 1.40).			
Steel.	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
G.....	0.730	0.007	0.737
I27 .....	1.023	0.013	1.036
I29 .....	0.872	none	0.872
I30 .....	0.675	none	0.675
I28.....	0.98	none	0.98
I32 .....	0.554	none	0.554
I32 .....	0.571	none	0.571
With fresh potash (sp. gr. 1.40).			
I33 .....	2.452	0.039	2.491
I34 .....	2.447	0.044	2.491
I35 .....	0.855	none	0.855
I.054 standard .....	1.033	0.030	1.063
I36 .....	0.906	0.023	0.929
I37 .....	1.301	none	1.301
With fresh potash (sp. gr. 1.40).			
I38 .....	1.298	none	1.298
I39 .....	0.98	none	0.98
I38 .....	1.27	none	1.27
I .....	1.167	none	1.167
2 .....	1.122	none	1.122
3 .....	1.101	none	1.101
4 .....	0.957	0.008	0.965
5 .....	1.116	none	1.116
With fresh potash (sp. gr. 1.40).			
6 .....	0.959	none	0.989
a6 .....	1.127	0.019	1.146
a1 .....	0.984	none	0.994
a5 .....	1.00	0.015	1.015
a3 .....	1.052	none	1.052
Gin saw.....	0.89	none	0.89

The reason why one set of potash bulbs always suffices to absorb all the carbon dioxide in the dry combustion process,<sup>1</sup> and does not apparently always suffice in the wet combustion method, is doubtless that in the former way the evolution of the carbon dioxide is gradual and the gas largely diluted with oxygen, while in the wet combustion method the carbon dioxide is perhaps given off all at once in the beginning of the process, and hence in a state of greater purity and concentration. Results by the lead chromate method in the preceding table

<sup>1</sup> Dr. Drown, and doubtless many other chemists, by many experiments, has found this to be the case, and with the extensive use made of this method of combustion any tendency to loss in this manner could not have escaped notice.

indicate that when the carbon dioxide is given off almost pure and undiluted, the tendency of the gas to escape complete absorption by the potash bulbs is very great.

But in using potash of specific gravity 1.40, it is seen that the amount of carbon dioxide absorbed by the second set of bulbs is usually very small if any, and this small increase of weight is probably in very many cases not due to carbon dioxide but to moisture, for there is a certain quantity of moisture uniformly escaping absorption by the drying train. The drying train consists in this case of a Liebig bulb with strong sulphuric acid, then a large U-tube filled with calcium chloride followed by potash bulbs with strong sulphuric acid. The unabsorbed moisture is consequently caught, or partly caught, by the absorption apparatus, and constitutes almost, if not quite, the entire "dummy" to be deducted from the result in an ordinary determination. And the amount of the moisture so escaping the drying train, and absorbed, or partly absorbed, by the two sets of potash bulbs and prolongs, although pretty uniform and unvarying in total amount as shown by blank tests, is nevertheless varying as regards the proportion absorbed by each absorption set. Results are shown by the following tests made in blank, with the same amount of reagents, etc., as in a regular test.

	First set of bulbs and pro- long. Equiva- lent to carbon. Per cent.	Second set of bulbs and pro- long. <sup>1</sup> Equiva- lent to carbon. Per cent.	Total moisture equivalent to carbon. Per cent.
One-half hour's aspiration ..	0.015	0.060	0.075
“ “ “ ..	0.051	0.016	0.067
“ “ “ ..	0.060	0.019	0.079
“ “ “ ..	0.056	0.015	0.071
“ “ “ ..	0.076	0.005	0.081
“ “ “ ..	0.055	0.013	0.068
“ “ “ ..	0.061	0.020	0.081
“ “ “ ..	0.055	0.026	0.081
“ “ “ ..	0.030	0.028	0.058
“ “ “ ..	0.041	0.031	0.072
One-fourth hour's aspiration.	0.041	0.028	0.069
“ “ “ ..	0.049	0.020	0.069
“ “ “ ..	0.019	0.046	0.065
“ “ “ ..	0.024	0.040	0.064
“ “ “ ..	0.036	0.028	0.064
“ “ “ ..	0.035	0.024	0.059

<sup>1</sup> Also weighed strong sulphuric acid bulb to this set.

*Fresh sulphuric acid in drying train.*

	First set of bulbs and pro- long. Equiva- lent to carbon. Per cent.	Second set of bulbs and pro- long. <sup>1</sup> Equiva- lent to carbon. Per cent.	Total moisture equivalent to carbon. Per cent.
One-fourth hour's aspiration.	0.047	—0.006	0.041
" " "	.. 0.052	0.016	0.062
" " "	.. 0.048	0.019	0.067
" " "	.. 0.039	0.021	0.060
" " "	.. 0.000	0.057	0.057

That these gains in weight are due mainly if not quite to moisture that the drying train failed to absorb, is shown by the following tests in which purified air was simply aspirated through the apparatus for about the same length of time, and as nearly as possible at the same rate of speed as the gas is evolved and air aspirated in an ordinary test.

	First set.	Second set.	Total moisture.
One-half hour's aspiration .....	0.058	0.000	0.058
One-fourth " " .....	0.038	0.026	0.064
" " " .....	0.032	0.044	0.076
Five minutes' aspiration .....	0.012	0.033	0.045

It is seen that there may be, in different determinations, considerable variation in the proportion of moisture absorbed by each set of bulbs, although the total amount is usually 0.065 per cent. in terms of carbon, or quite close to it. So in deducting "dummies" from each set of bulbs, this variation may cause an absorption of carbon dioxide to be indicated by the second set of bulbs, when in reality the gain in weight of this set of bulbs may be due merely to a variation in moisture from the "dummy" subtracted. The results with use of potash of 1.40 specific gravity therefore do not prove, when the amount of carbon is not unusually large, and the potash solution not too long in use, that one set of bulbs, using potash of that strength, is insufficient. These results, and the dummy results following, indicate very plainly, however, the necessity for using more than one drying apparatus after and with the potash bulbs. Mr. David H. Browne, in his admirable "Hints to Beginners" in *Journal of Anal. and Appl. Chem.*, speaks of this in connection with the wet method, although the necessity of it is perhaps not generally recognized. But there is some little difference of opinion among chemists who use the other (dry) method of combustion;

<sup>1</sup> Also weighed strong sulphuric acid bulb to this set.

Dr. Drown, for instance, has found a single prolong filled with calcium chloride sufficient to catch all the moisture from the potash bulbs. On the other hand Mr. Andrew A. Blair has noticed a loss of moisture from the prolong; and Dr. Dudley also hints at the same thing, and thinks it probable that "some of the difficulty in getting absolute blanks may be accounted for in this way." It is not strange that in the dry method with a careful performance of the operation there should be, with some manipulators, a complete absorption of the moisture by the prolong. But in the wet method where the evolution of gas is more abundant and longer continued, it is the writer's experience, at least, that the prolong filled with freshly dried calcium chloride usually falls very short of absorbing all the moisture from the potash bulbs, the moisture thus lost amounting sometimes to as high as 0.14 per cent. in terms of carbon with one-half hour's aspiration.

But the escape of moisture from the prolong would be of no serious consequence (if dummy tests were carefully made) provided the moisture so escaping was invariably uniform in amount. The following tests, however, show a very great lack of uniformity in this respect and illustrate the necessity, in the wet method, of having more than the usual drying agencies after the potash bulbs to insure a uniform though probably still not complete absorption of the moisture from the potash bulbs. In these tests the moisture lost from the prolong was determined by absorbing it in a weighed potash bulb following and connected with the prolong, and having the two anterior bulbs filled with strong sulphuric acid. The results are consecutive, and are expressed in terms of carbon per cent:

One-fourth hour's aspiration—equivalent to carbon, per cent.: minus 0.005 per cent.; plus 0.004 per cent.; 0.004 per cent.; 0.004 per cent.; 0.002 per cent.; 0.015 per cent.; 0.008 per cent.; 0.010 per cent.; 0.019 per cent.; 0.017 per cent.; 0.013 per cent.; 0.023 per cent.; 0.021 per cent.; 0.026 per cent.; 0.021 per cent.; 0.048 per cent.; 0.062 per cent.; 0.060 per cent.; 0.062 per cent.; 0.058 per cent.; 0.060 per cent.; 0.052 per cent.

With fresh calcium chloride in prolong: 0.015 per cent.; 0.003 per cent.; 0.018 per cent.; 0.012 per cent.; 0.015 per cent.; 0.000 per cent.; 0.018 per cent.; 0.015 per cent.; 0.010 per cent.; 0.009 per cent.

With fresh calcium chloride, and one-half hour's aspiration: minus 0.006 per cent.; 0.005 per cent.; 0.015 per cent.; 0.023 per cent.; 0.018 per cent.; 0.018 per cent.; 0.012 per cent.; 0.018 per cent.; 0.027 per cent.; 0.032 per cent.; 0.010 per cent.; 0.006 per cent.; 0.016 per cent.; 0.012 per

cent.; 0.020 per cent.; 0.025 per cent.; 0.022 per cent.; 0.016 per cent.; 0.022 per cent.; 0.028 per cent.; 0.044 per cent.; 0.049 per cent.; 0.076 per cent.; 0.077 per cent.; 0.071 per cent.; 0.055 per cent.; 0.046 per cent.; 0.053 per cent.; 0.119 per cent.; 0.138 per cent.; 0.074 per cent.; 0.081 per cent.; 0.065 per cent.; 0.053 per cent. Then with one-fourth hour's aspiration 0.043 per cent.; 0.052 per cent.; 0.050 per cent.; 0.042 per cent.; 0.081 per cent.; 0.050 per cent.; 0.043 per cent.; 0.043 per cent.; 0.046 per cent.; 0.029 per cent.

The sulphuric acid bulbs in their turn doubtless let some moisture through ; but that by their use in connection with the prolong uniformity is obtained, is shown by the dummy results already given.

It is not supposed that the prolong and the sulphuric acid bulbs together absorb absolutely all the moisture from the potash bulbs for the reason that the drying train before the potash bulbs, consisting of two sulphuric acid bulbs, and one large calcium chloride tube, allows moisture equivalent to 0.065 per cent. carbon to escape in the course of a determination and therefore the drying apparatus after the potash bulbs doubtless also allows moisture to escape.

The writer is inclined to think that no apparatus now used in the absorption of moisture in the carbon process will absorb the moisture completely when the flow of gas is brisk and continued as in the wet method. Mr. A. A. Blair considers anhydrous copper sulphate an excellent absorbent of moisture. In fact it dries the gas too thoroughly; so that, as Mr. Blair says, "the gas leaves the prolong with more moisture than when it entered the absorbing apparatus." He therefore places a plug of moist cotton wool after the copper sulphate in the drying train and before the calcium chloride tube of the drying train in order to secure a uniformity of conditions in this particular. The loss of moisture from the prolong is thus equalized by a gain of moisture from the calcium chloride tube of the drying train. In this connection it is interesting to note a difference of opinion between Mr. Blair and Dr. Drown and others. Dr. Drown says that he finds no advantage in the use of the plug of moist cotton wool. Mr. Shimer, Dr. Dudley, and others seem to find no occasion for its use. As the only difference between the apparatus of Messrs. Drown, Dudley, and Shimer on the one hand, and Mr. Blair on the other (excepting the preheating furnace), is that the



former contains ferrous sulphate solution in the train immediately preceding the copper sulphate tube, it would seem a plausible inference that in the former case a plug of moist cotton wool, before the calcium chloride train is not needed because the moisture from the ferrous sulphate solution supplies the amount necessary to counterbalance that lost from the prolong—the anhydrous copper sulphate intervening in Messrs. Drown and Shimer's apparatus being in that case not so good a drying agent after all.

However easy and tempting this deduction may be, it is nevertheless inadmissible from the simple fact that Dr. Drown finds that no moisture at all escapes from the prolong in his use of it. Hence the only explanation left us for the fact that Mr. Blair finds the use of moist cotton wool necessary or advisable and Messrs. Drown, Dudley, and Shimer do not, is of course the simple one that in the one case the passage of gas and the aspiration of air is allowed to proceed more gently than in the other, so that in this case moisture is neither drawn from the drying train on the one hand, nor lost from the prolong on the other. This is of course a perfectly reasonable supposition, but if a difference in manipulation merely (and probably a slight difference) is responsible for this difference in behavior, then it would seem best for the ordinary operator to be on the safe side by assuming that moisture does escape from the prolong, and to proceed accordingly.

The writer nevertheless ventures to question whether there is any real need of introducing the moist cotton wool into the apparatus—whether, in fact, it is not distinctly inadvisable so to do. For, the less moisture carried into the weighed absorbing apparatus, the less variable will obviously be the amount of moisture escaping from it and the less, therefore, “the difficulty of obtaining absolute blanks,” and the more concordant the results. If more moisture escapes absorption by the prolong than is gained from the drying train, and the dummy is therefore a minus quantity, so much the better, showing, as it does, that the drying train is a good one and allows but little moisture through it. And it is just as easy to apply a plus correction to the result in a regular determination as a minus one; that is, if our dummy is minus we add instead of subtracting it from our results. The important matter is, of course, to get an absolute

dummy—one that does not vary, and the writer therefore thinks it better still to use a weighed sulphuric acid bulb or some other additional drying apparatus after the prolong to secure this uniformity until convinced by many such trials that (in the operator's manner of procedure) no moisture escapes absorption by the prolong. For the writer, moisture does escape from the prolong, in the dry as well as in the wet method of combustion, varying in the dry method from 0.000 per cent. to 0.08 per cent. in terms of carbon, according to the freshness of the calcium chloride, its state of division, and the speed of aspiration. In using calcium chloride Dr. Dudley directs that it be freshly dried before use. This is such a necessary precaution as to bear much iteration.

A calcium chloride tube filled directly from a half-emptied bottle and therefore without previous drying lost by aspirating dry air through for two hours, equivalent to carbon: 0.047 per cent.; repeated, lost 0.14 per cent.; again, gained 0.02 per cent.; again, lost 0.19 per cent.; again, lost 0.48 per cent.

A wash-bottle with water was followed by this calcium chloride, and that in its turn by a weighed sulphuric acid bulb. The bulb gained in weight 0.32 per cent. and 0.29 per cent., so that the drying of the calcium chloride previous to use is an absolutely necessary precaution.

It seems to be necessary with some potash solutions to aspirate air through before using. Several blank tests made without doing this showed a loss of weight, in the one case equal to 0.048 per cent. carbon and in the other 0.019 per cent. carbon.

In the writer's experience a most serious difficulty with the wet method of combustion is, that occasionally results are obtained from 0.05 to 0.07 per cent. above the truth, due apparently to some chloro-chromic compound other than that absorbable by Prof. Langley's "pyro" mixture. At least the writer can offer no other explanation, the purifying train including: water kept cold for hydrochloric acid according to Porter Shimer; ferrous sulphate for chlorine according to Dr. Dudley; "pyro" mixture for chlorine, oxides of chlorine, and chloro-chromic anhydride according to Prof. Langley; and silver sulphate in strong sulphuric acid for hydrochloric acid.

It is known that the wet method is unsuited for graphite de-

terminations owing to a portion of the graphite being oxidized merely to carbon monoxide.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 30.]

## COMPARISON OF THE STANDARD METHODS FOR THE ESTIMATION OF STARCH.<sup>1</sup>

BY H. W. WILEY AND W. H. KRUG.

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THE study of the nature of the carbohydrate bodies which exist in foods has been vigorously prosecuted by chemists in different parts of the world during the past few years. The result of these studies has been to arouse new interest in the standard methods of starch determination. The numbers which are secured by different workers for starches vary so greatly as to lead to the belief that the estimation of starch is not such an easy matter as is generally supposed; in fact, long experience has convinced us that there are few operations in agricultural analytical chemistry which require greater skill, or are attended with greater difficulties than the estimation of starch in the presence of the other carbohydrate bodies.

At a recent meeting of chemists in England, it was stated in one of the papers that the methods of starch determination are now so easy of application and so accurate that there is no longer any excuse for being ignorant of the exact content of starch in any body. Stone, in Bulletin No. 34 of the Office of Experiment Stations, described a method which was easily seen to be erroneous, yielding only about half as much starch as was really contained in the samples examined. A cursory glance at the methods of analysis employed by him convinced us that the fault was insufficient saccharification, due to the weakness of the acid and the shortness of the time of heating.

In a subsequent article<sup>2</sup> Stone called attention to the error of his previous statements, and proposed a modification of his first published method, which, as is seen below, gives very much better results. Having to estimate, annually, the starches in many hundreds of substances, we were led to make a compara-

<sup>1</sup> Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.

<sup>2</sup> This Journal, 19, 347.

tive study of the standard methods which have been used for starch determination, and of some modifications which seemed to us worthy of trial. The standard methods which we employed were those described in "Principles and Practice of Agricultural Analysis," 3, 196-222, and 300-302. The materials which we used in our investigations were starches of commerce, the ordinary cereal grains, and a sample of the wheat which was the subject of the investigations of Stone, and which was kindly furnished us by Professor Stone. We give below a brief résumé of the work we have done.

The sample of spring wheat No. 1, which we received from Professor Stone, was examined for all of its principal constituents, according to the official and standard methods of analysis, and the data obtained by him and by us are given below. The moisture stated in the second column of the appended table was determined by drying for five hours in a high vacuum at 100°.

#### PRELIMINARY GENERAL ANALYSIS.

Spring wheat No. 1.	Data obtained by	
	Stone. Per cent.	Wiley and Krug. Per cent.
Moisture .....	8.55	10.65
Ether extract.....	2.00	2.24
Ash ....	1.43	1.77
Fiber.....	2.77	2.56
Albuminoids .....	14.22	14.44
Pentosans .....	4.54	5.17
Starch and undetermined.....	66.49	63.17

Before determining the starch it seemed of interest to take the sample in the state in which it was sent, as we assumed that it had thus been analyzed by Professor Stone. It also seemed to us that the digestion with malt extract prescribed by him was not long enough to insure the complete conversion of the starch into maltose and dextrins. To determine this, one set of samples was digested one hour at 60°, and another set two and one-half hours at 50°, since Lintner states that diastase is most active at this latter temperature. The results obtained show that our surmise was correct.

Spring wheat No. 1.	Stone method. Per cent. of starch,	Wiley and Krug method. Per cent. of starch.
<i>a</i> .....	56.27	57.39
<i>b</i> .....	57.00	58.73
<i>c</i> .....	58.65	59.88
Means.....	57.31	58.66

The residues from the diastase digestion were all thoroughly washed with hot water and then examined with iodine under the microscope. In every case a large number of cells was found which contained undigested starch, showing that the sample had not been ground to a sufficient degree of fineness. This is, therefore, another source of error in Professor Stone's work. The sample was then reground and the starch determined by three methods; *viz.*, first, the Reinke lactic acid method, second, a method which differs from this by the use of five-tenths gram of salicylic acid instead of lactic acid, and third, the diastase method. The residues were again examined and in every case found free from starch, showing that the conversion had been complete.

The following results were obtained :

Spring wheat No. 1.	Reinke method. Per cent. of starch.	Salicylic acid method. Per cent. of starch.	Diastase method. Per cent. of starch.
<i>a</i> .....	62.22	63.25	62.66
<i>b</i> .....	62.41	63.09	62.25
<i>c</i> .....	....	62.94	....
Means .....	62.32	63.09	62.46

As is subsequently shown, the result obtained by the last method is more probably correct. The number for starch thus obtained, added to our per cents. of the other constituents gives us a total of 99.28. The separate determination of the sucrose, galactan, invert sugar, and dextrin, originally present, was omitted, and these bodies are included with the starch.

This work led us to undertake an investigation of other methods for the determination of starch which have been proposed from time to time, our desire being to avoid, if possible, the use of diastase and to shorten the time of procedure.

It seemed that this might be accomplished by polarizing the

products of hydrolysis and thus avoiding the labor incident to the gravimetric method of determining copper. To this end, several methods were tried. These methods depend either on the complete conversion of the starch into dextrose or on the formation of soluble starch, maltose, and dextrans.

#### THE GUICHARD METHOD.

Guichard<sup>1</sup> proposes to boil four grams of the material for one hour with 100 cc. of ten per cent. nitric acid (ten cc. strong acid (sp. gr. 1.42). to ninety cc. water) in a flask provided with a return condenser. The solution is cooled, filtered, and polarized. The starch is found by the formula

$$A = \frac{av \times 25 \times 0.016}{2 \times 52.8},$$

where  $a$  = rotation in angular degrees,  $v$  = volume of liquid, and  $A$  = starch transformed. As our polarizations were made with a Schmidt and Haensch instrument, the dextrose was determined by the formula

$$(a)_D = \frac{a \times 100}{c \times l},$$

where  $a$  = rotation,  $c$  = weight of dextrose,  $l$  = length of tube in dm., and  $(a)_D = 52.8^\circ$ .

#### THE PRESSURE METHOD.

Three grams of substance are heated in a flask with eighty to ninety cc. of water until pasty, and the starch rendered soluble by heating from three to five hours in an autoclave, at from two to three atmospheres. The volume is completed to 100 cc. and the solution polarized. The gyrodynat of soluble starch prepared in this way varies from  $(a)_D = 196.5^\circ$  to  $197^\circ$ .

#### THE BAUDRY METHOD.

To 2.883 grams of the substance (for Schmidt and Haensch instrument) add from eighty to ninety cc. of water and five-tenths gram salicylic acid. Boil twenty minutes, dilute to about 190 cc., add one cc. ammonia, cool, dilute to 200 cc., filter, and polarize in a 400 mm. tube. Multiply the result by three. Baudry determined the gyrodynat of soluble starch to be  $(a)_D =$

<sup>1</sup> This and the following polarimetric methods are described in detail in Vol. III of "Principles and Practice of Agricultural Analysis."

202.66° at 15°–18° C., when sucrose = 67.3° (Girard and de Lugnes), and 200.25° when sucrose = 66.5° (Tollens). As the normal weight for sugar is 26.048 grams ( $(\alpha)_D = 66.5^\circ$ ) the normal weight for starch will be  $\frac{26.048 \times 66.5^\circ}{200.25^\circ} = 8.650$  grams.

We furthermore tried to apply polarization to the solution obtained by the Reinke method. Three grams of the material were heated two and one-half hours in the autoclave with thirty cc. of one per cent. lactic acid and 25 cc. of water at three and one-half atmospheres, diluted to about eighty cc. and inverted two and one-half hours with five cc. hydrochloric acid of 1.20 specific gravity. The volume of the solution was then completed to 100 cc., filtered, and polarized. The results show that the polarizing power of the solution was too high and that too little acid had been used, and another series was made in which the quantity of acid was doubled. In this case, the results were too low. The solutions were always highly colored, and we were unable to polarize them without previous treatment with bone-black. In the following table are given the results obtained by the polarimetric methods above described.

Nos. 1 and 2 are samples of commercial corn starches, Nos. 3 and 4 specimens of wheat obtained at the Columbian Exposition.

#### COMPARISON OF POLARIMETRIC METHODS ON STARCH AND WHEAT.

	Guichard method. Per cent. starch.	Pressure method. Per cent. starch.	Baudry method. Per cent. starch.	Reinke method. Five cc. acid. Per cent. starch.	Reinke method. Ten cc. acid. Per cent. starch.
1. Starch .....	81.9	....	67.8	100.16	76.33
	80.04	....	....	101.26	76.33
	80.90	....	....	....	....
Means..	80.97	....	....	100.71	76.33
2. Starch .....	83.72	....	80.4	101.81	79.73
	84.18	....	....	102.90	76.33
Means..	83.95	....	....	102.36	78.03
3. Wheat .....	55.43	36.45	28.89	83.45	50.35
	55.94	41.66	....	82.26	49.86
Means..	55.69	39.06	....	82.66	50.11
4. Wheat .....	53.59	36.45	36.00	96.56	49.62
	53.13	36.45	35.46	92.99	49.34
Means..	53.36	36.45	35.73	94.78	49.48

This table shows that there is much variation between the results obtained by the different methods. The Guichard method gives promise of being applicable to pure starches, but does not give good results with wheat. When the nitric acid is added to the cereal the oxidizing action is very violent for some minutes, and the proteid matters which are brought into solution doubtless counteract, to some extent, the right-handed rotation due to the dextrose formed. It is evident also that the acid brings a large proportion of the pentosans into solution. It seems probable that a careful study of the conditions under which the Reinke method should be used may render this method available. The pressure method fails to render all the starch soluble, as was shown in the work with pure starch, where in every case the solution contained large quantities of gelatinized starch, which made filtration and polarization almost impossible.

The use of salicylic acid in the Baudry method suggested its substitution for lactic acid in the Reinke method, as it was noticed that the solutions obtained with it were very free from caramelization. It was found that this was also true of the solutions obtained with it in the autoclave. The results were proportionately higher and indicate that lactic acid in conjunction with the pressure decomposes a considerable portion of the pentosans present. Comparative estimations on the same samples gave the following results:

Material.	Lactic acid. Per cent. starch.	Salicylic acid. Per cent. starch.
1. Starch .....	82.93	84.27
2. Starch .....	82.60	84.03
3. Cornstarch.....	<i>a</i> 83.96	<i>a</i> 84.27
	<i>b</i> 83.66	<i>b</i> 84.46
	<i>c</i> 83.84	<i>c</i> 84.21
	<i>d</i> 83.72	<i>d</i> 84.24
	<hr/>	<hr/>
Means.....	83.795	84.295
4. Wheat .....	62.25	63.17
5. Wheat .....	62.32	63.09

These figures show a fairly uniform increase in the amount of starch found when salicylic acid was used. It might be claimed that this increase in the case of wheat is due to the greater solubility of the pentosans present in the cereal and not to the greater solvent power of the salicylic acid on starch. In order



to determine whether this is the case, three grams of wheat were treated in the autoclave by two methods, 100 cc. of the filtrate distilled with twelve per cent. hydrochloric acid and the furfural determined. It was found that lactic acid dissolved 3.55 per cent. of pentosans and salicylic acid 3.69 per cent. in terms of the substance. It is therefore evident that both acids exert a like hydrolyzing power on the pentosans and the increased percentage of starch by salicylic acid is not due to this property. The solutions obtained with salicylic acid were never at any stage of the process darker than a straw-yellow while the final liquid obtained with the Reinke method is generally deep brown, showing that considerable caramelization has taken place. We therefore recommend the use of salicylic acid in place of lactic acid when it is necessary to determine the fermentable constituents of a cereal by the high pressure method, and also with the proper corrections for general analytical work.

#### METHOD OF LINDET.

Lindet<sup>1</sup> describes the following method for the direct determination of starch.

According to an observation of Girard, the grains of starch in the cereals are surrounded with a glutinous envelope, and the principle of the new process of Lindet is based upon the solution of this envelope by pepsin under such conditions as to prevent any hydrolysis of the starch. After the solution is complete, the starch granules are easily washed out, collected, dried, and weighed. The process is therefore one for the direct determination of starch, and gives promise of usefulness in the technical examination of cereal grains to be used for starch-making. The cereal grains are finely ground and ten grams of the flour are placed in a vessel and covered with a solution containing two per cent. of pepsin and one and one half per cent. of hydrochloric acid. The mixture is left for twelve or fourteen hours, with frequent shaking, at a temperature of from 40° to 50°. The contents of the vessel are then poured upon a fine bolting-cloth, the cloth gathered into the form of a knot and washed in a capsule of water until starch is no longer removed. The washwaters containing the starch are brought together, treated with

<sup>1</sup> Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie, 14. 405

a little formic aldehyde or mercuric chloride to prevent bacterial action, and the starch is collected upon a weighed filter. The filtration is somewhat tedious, especially when the cereal contains large quantities of gum. It can be facilitated, to a certain degree, by adding to the filter a known quantity of calcined and washed pumice stone. The collected starch is dried at first at 50° and finally at 150°. Lindet has assured himself, by careful trial, that the presence of the hydrochloric acid in the quantity noted above prevents the action of any of the natural diastases or enzymes which the cereal may contain upon the starch, but that a hydrochloric acid of that strength exercises, at the temperature employed, no hydrolyzing effect whatever upon the starch granules.

The method appeared to be so short and easy of manipulation that we decided to try it. For this purpose four cereals were purchased and prepared; *viz.*, wheat, oats, rye, and barley. A general analysis was first made which gave these results:

	Wheat. Per cent.	Rye. Per cent.	Oats. Per cent.	Barley. Per cent.
Moisture.....	11.33	11.71	9.26	12.20
Ether extract .....	2.00	1.63	4.72	0.92
Fiber .....	2.15	2.36	12.81	0.80
Ash .....	1.69	2.31	3.78	0.93
Proteids.....	12.19	11.69	9.63	10.44
Pentosans .....	5.80	8.10	13.65	6.50
(a) Starch <sup>1</sup> (salicylic acid method).....	64.41	62.64	46.78	68.38
(b) Starch <sup>1</sup> (diastase method).....	63.17	61.55	45.05	67.56
Total (including starch a)	99.57	100.44	100.63	100.17
Total (including starch b)	98.33	99.35	98.90	99.35

The starch was determined both by the use of salicylic acid as described above and by the means of diastase. The increase due to the hydrolyzing action of the acid is clearly shown by the data and proves that its use as well as that of other organic acids is warranted only when analytical data are desired in connection with the technical use of high pressure in commercial operations, or when the final data are corrected as hereinafter described.

<sup>1</sup> Including sugar, galactan, dextrin, etc.

In our application of the Lindet method to these cereals we reduced the amount taken to three grams, as it seemed desirable to estimate the starch not only by direct weighing but also after conversion into dextrose, and this quantity was found very convenient to handle on the bolting-cloth. The starch was also determined in the residue left on the cloth, and the starch which was washed through was dried and weighed, then gelatinized, treated with malt extract, and determined as usual. It was then found that in most cases some fiber had gone through the cloth and rendered the results too high.

## LINET METHOD.

Cereal.	Direct weight.			Determination after conversion into dextrose.			
	Starch. Per cent.	Residue. Per cent.	Total. Per cent.	Starch. Per cent.	Residue. Per cent.	Total. Per cent.	Fiber in starch. Per cent.
Oats . . . . .	44.19	0.14	44.33	44.27	0.14	44.41	. . . .
	44.31	0.00	44.31	43.73	0.00	43.73	0.58
	43.81	0.33	44.14	43.47	0.32	43.80	0.34
Barley . . .	71.41	0.97	72.38	66.47	0.97	67.44	4.94
	72.72	0.00	72.72	67.47	0.00	67.47	5.25
	71.66	0.98	72.64	66.51	0.98	67.49	5.15
Rye . . . . .	61.24	0.79	62.03	58.18	0.79	58.97	3.06
	60.83	1.21	62.04	57.94	1.21	59.15	2.89
	59.83	2.41	62.24	57.68	2.41	60.09	2.15
Wheat . . .	67.35	0.00	67.35	60.18	0.00	60.18	7.17
	66.05	0.60	66.65	60.11	0.60	60.71	5.94
	66.55	0.00	66.55	60.26	0.00	60.26	6.29

This table shows that not quite all the starch was removed by the washing in every case, and that some material which is not starch is counted as such. It required almost a week to filter the liquid containing the starch and this was no doubt due to the pepsin present. It was also quite impossible to keep some of the starch granules from running through the filter. The method is therefore more tedious than the common processes and not nearly so accurate.

One of the main sources of error in the estimation of starch in a cereal is the difficulty of converting it all into soluble products. This is due to the fact that the starch granules are imbedded in proteid matters and are thereby partially protected from the action of the solvent. We have therefore combined the use of pepsin to dissolve this protein with the salicylic acid method

described above. Three grams of the cereal were digested fourteen hours at 45° C. with thirty cc. of pepsin solution, the hydrochloric acid carefully neutralized with sodium carbonate, five-tenths gram salicylic acid added, and the material heated two and one-half hours in the autoclave to three and one-half atmospheres. The neutralization of the hydrochloric acid is necessary, since it would dissolve additional quantities of the pentosans present. Some curious color-reactions took place during the process. The neutralization with sodium carbonate turned the solution light green. On removal from the autoclave it was found to be a straw-yellow, but after neutralizing the hydrochloric acid used in the final inversion the liquid again became deep green. This is probably due to the products formed by the action of the pepsin on the proteids. The results obtained follow :

	Starch.			Means. Per cent.
	Per cent.	Per cent.	Per cent.	
Wheat .....	64.50	64.51	64.44	64.48
Rye.....	62.41	62.14	62.50	62.35
Oats .....	47.29	47.42	47.08	47.26

A comparison of these results with those obtained by the salicylic acid method alone shows a close concordance. The use of pepsin is, however, a safeguard which it is well always to apply as it insures the thorough solution of the starch. The pepsin must be free from material which exercises a reducing action on the copper solution. We have also tried the combination of the pepsin and diastase digestions, but reserve the report on this method for further study.

We also have thought it advisable to apply taka-diastase instead of malt extract for dissolving the starch, since it can easily be obtained in a dry form and retains its activity for a considerable length of time. We were not able to study its action thoroughly on account of lack of time, but found that five-tenths gram of taka-diastase required twelve hours to completely dissolve the starch in three grams of wheat. The experiment was made at 50°. It was found that the taka-diastase contained no reducing substances, which is an advantage over malt extract. The solutions obtained with it had commenced to decompose at

the end of twelve hours and it was therefore deemed inadvisable to estimate the starch in them.

We have also tried quite extensively the pancreatic diastase prepared by Frederick Stearns & Co., of Detroit, and found it exceedingly active and free of any reducing matter. The indications are that it may prove to be the most desirable form of hydrolyzer yet used. The data obtained by us with this reagent will be increased and made the subject of another communication.

Following are the conclusions which are drawn from the vast amount of analytical data which has been accumulated.<sup>1</sup>

1. All the heretofore described methods for determining the percentage of starch by polarization, whether with the soluble starch or with dextrose made therefrom, are liable to grave errors and none of them can be relied upon to give accurate results. The only advantage which can be claimed for such methods is in the saving of time. The sources of error, however, are so great as to nullify the advantage of time-saving.

2. The methods depending upon hydrolysis in an atmosphere of steam under pressure are obnoxious to the danger of caramelization. This seems to be entirely prevented by the addition of a very small quantity of an organic acid. Of the organic acids suggested tartaric is excluded on account of its optical properties. Of lactic and salicylic acid the latter is to be preferred. In all cases where dilute organic acids are employed the pentosans of the cereal and its products are hydrolyzed to a considerable extent. The presence of the sugars produced by the hydrolysis of the pentosans increases the quantity of metallic copper obtained and thus raises the apparent percentage of starch. In these cases, a correction must be made by determining the quantity of pentose sugar present and diminishing the percentage of starch obtained in proportion to the quantity of pentose sugar found.

In this instance, a difficulty arises from the uncertainty concerning the quantity of pentosan corresponding to a given amount of sugar produced therefrom reckoned as dextrose. We have seen

<sup>1</sup> More than 500 gravimetric determinations have been made by Mr. W. H. Krug in prosecuting this research. In each case the reduced cuprous oxide was dissolved and the metallic copper precipitated electrolytically.

that salicylic acid, in the autoclave, under the conditions specified above, dissolved 3.69 per cent. of pentosans calculated on the weight of the ground cereal employed. We have shown in another paper that diastase dissolves very little pentosan from cereals. It is therefore easy to make a determination of the copper reducing power of the dissolved pentosans reckoned in terms of dextrose. In a preceding table, we have shown the excess of reducing sugar, obtained by the salicylic acid under pressure, over the amount secured by the diastase method without pressure. In the case of wheat this excess was 1.24 per cent., in rye 1.09 per cent., in oats 1.73 per cent., and in barley 0.82 per cent.

The mean excess for the four cereals examined was 1.23 per cent. In the case of wheat, therefore, it is seen that 3.69 per cent of dissolved pentosans yielded an amount of reducing sugar equivalent to only 1.24 per cent. of dextrose. We therefore propose, in the case of wheat, when the salicylic acid method is used with pressure in the autoclave, to diminish the apparent per cent. of starch by 1.25. Where greater exactitude is required the pentosans should be determined and the per cent. found divided by three. The quotient will be the figure to be subtracted from the apparent percentage of starch obtained.

3. The direct weighing of the starch, according to the method of Lindet, after solution of the protein by means of pepsin, has many advantages for practical work, especially in starch factories. Small particles of other matters, however, of no greater size than the starch grains themselves, pass through the bolting-cloths and are reckoned as starch in the final weighings. This error is partly compensated for by a portion of the starch remaining attached to the filter and the final result by the Lindet method is in some cases approximately correct.

4. The combination of the Lindet method, in so far as the solution of the protein is concerned, with the diastase method as practiced by us, has given most encouraging results and it is probable that a satisfactory method of starch estimation can be worked out in this line.

5. The diastase method without pressure gives satisfactory results when the diastase is freshly prepared and used in proper quantities and at an appropriate temperature. The diastase

exerts only a small solvent action on the pentosans and the final hydrolytic products obtained are not contaminated with any appreciable amounts of pentose sugars. The use of taka-dias-tase is worthy of further investigation since it can be easily prepared uncontaminated with any reducing sugars. The sample we employed, however, was not very active, requiring several hours more time for a complete solution of the starch than diastase recently prepared from malt. The materials on which the diastase acts should be ground to the finest possible powder and should be previously extracted with ether to prevent the retarding action of fat on the ferment. The treatment with diastase should always be repeated after boiling and cooling to about 50°. The residue must not show any starch granules when stained under the microscope with iodine.

6. The time at our disposal did not permit us to make a comparative trial of saliva as a solvent for the starch. This part of the problem remains to be worked out, and it is hoped that saliva will be found to exert a minimum solvent action on the pentosans and celluloses present in cereals.

7. The summation of the several per cents., obtained in the analysis of a cereal or cereal product by the methods employed by us, does not in all cases approximate closely to 100. The variations are somewhat greater than in ordinary mineral analysis. They are, however, not of such a magnitude as to warrant the assumption of the existence in cereals of a class of bodies of unknown properties and different in any marked degree from those already known to exist. In this connection, it should not be forgotten that in the estimation of the ash by the official method there is danger of loss of chlorine, sulphur, and phosphorus, especially of the former and latter, the organic phosphorus escaping combination with the already saturated bases present. In some recent experiments we have found the loss to be more than one per cent. of the total weight of the cereal employed. When this fact is taken into consideration, it is evident that there is practically no constituent unaccounted for in the analytical data. The small quantity of matter unaccounted for in the cereal grains is doubtless of a carbohydrate nature, belonging to that complex class, pentosan-ligno-celluloses, whose chemical and physical properties are so nearly alike as to make

their exact separation and determination extremely difficult. The quantity of these undetermined bodies in cereal grains is very minute. In stalks and straw, and other bodies containing a large excess of ligno-cellulose compounds, this quantity is doubtless much larger.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S DEPARTMENT OF AGRICULTURE, No. 31.]

## THE SOLUBILITY OF THE PENTOSANS IN THE REAGENTS EMPLOYED IN THE ESTIMATION OF STARCH.

BY W. H. KRUG AND H. W. WILEY.<sup>1</sup>

Received February 15, 1898.

THE methods which have been generally adopted for the quantitative determination of starch in a cereal or fodder are based on one or two principles; *viz.*, the application of high pressure in contact with water containing some organic acid, to prevent the decomposition of the sugars formed during the hydrolysis, or the conversion of the starch by means of diastase. The results obtained by the former methods are always a little too high and do not represent the actual starch content of the material under examination. In analytical work where it is desired to obtain the exact percentage of starch, diastase must be used and the application of any acid avoided until those bodies which may be acted upon by it have been removed by filtration, or else a correction must be applied as described in our preceding paper. The increased amount of starch found by the use of high pressure methods is due to the action of the organic acid on the pentosans and hemicelluloses present which results in the formation of reducing substances.

We have determined the amount of pentosans dissolved in the application of these methods with the following results:

1. Solubility of the pentosans by digesting for two and one-half hours at three and one-half atmospheres with thirty cc. of water and twenty-five cc. of one per cent. lactic acid:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved.	
		In per cent. of substance.	In per cent. of pentosans.
Wheat No. 1 . . . . .	5.80	4.63	79.83
Wheat No. 2 . . . . .	5.17	4.66	90.13

<sup>1</sup> Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.



2. Solubility of pentosans by digesting for two and one-half hours at three and one-half atmospheres with fifty-five cc. of water and five-tenths gram salicylic acid:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved.	
		In per cent. of substance.	In per cent. of pentosans.
Wheat No. 1 .....	5.80	4.54	78.27
Wheat No. 2 .....	5.17	4.08	78.91

The pentosans which had gone into solution were determined by diluting the liquid to 250 cc. after cooling, filtering, and distilling 100 cc. of the filtrate with twelve per cent. hydrochloric acid until no furfural could be detected in the distillate. The furfural was precipitated with phenylhydrazin acetate in the usual manner.

J. König, in an article on the methods of analysis used in the examination of fodders published in *Landwirthschaftlichen Versuchs-Stationen*, 48, 81, states that diastase also acts as a solvent for pentosans and hemicelluloses and gives the following figures:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved by diastase.	
		In per cent. of substance.	In per cent. of pentosans.
Rye .....	8.90	2.22	24.95
Peas .....	3.62	1.02	28.17
Potatoes .....	2.12	0.94	44.34
Rye straw .....	18.07	2.74	15.22
Pea straw ... ..	10.27	1.85	18.11

If this were true, it would render the diastase method fully as unreliable as the high pressure methods and the problem of determining the exact starch content of a material would be as far from solution as ever. We therefore decided to investigate this point with the following results:

Solubility of pentosans by digesting with thirty cc. malt extract (100 grams malt to one liter of water) until all starch had been converted:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved by malt diastase.	
		In per cent. of substance.	In per cent. of pentosans.
Wheat .....	5.80	0.011	0.181
Barley .....	6.50	0.010	0.151
Rye .....	8.10	0.016	0.195
		0.017	0.206
Oats .....	13.65	0.010	0.071
		0.010	0.071

Solubility of pentosans by digesting with five-tenths gram taka-diastrase until all starch had been converted:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved	
		In per cent. of substance	In per cent. of pentosans.
Wheat .....	5.80	0.011	0.194
		0.012	0.199
Barley .....	6.50	0.015	0.238
Rye.....	8.10	0.017	0.209
Oats .....	13.65	0.011	0.079

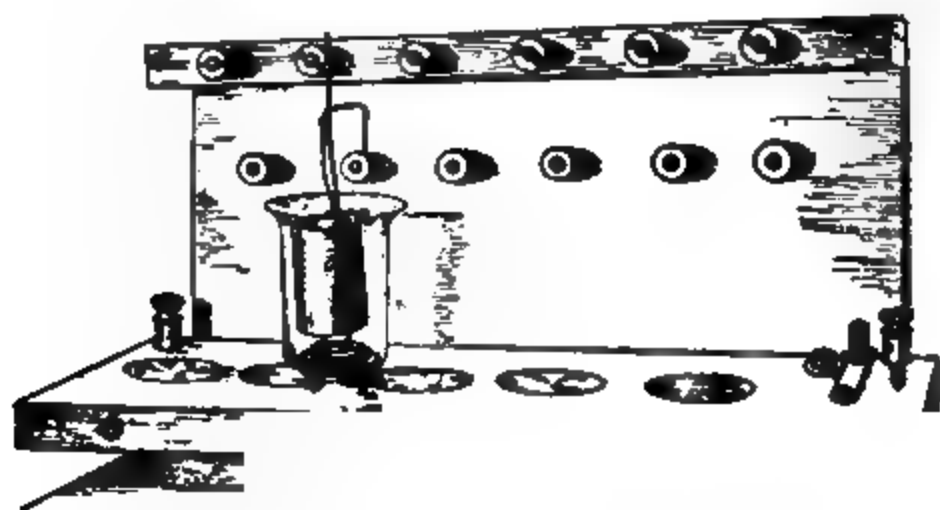
The small amounts of pentosans found here are, without doubt, not due to any solvent action of the diastase on the pentosans as it is well known that soluble starch, dextrin, sucrose, and all hexoses will yield small amounts of furfural when distilled with twelve per cent. hydrochloric acid. We are therefore justified in assuming that diastase has no solvent action on the pentosans and is a reliable means for determining the exact starch content of a cereal or fodder.

### A NEW ELECTROLYTIC STAND.

BY GEORGE J. HOUGH.

Received February 3, 1898.

THE electrolytic stand herein described was devised and made by myself, and is, as I believe, an entire novelty. It is very simple and easy of construction, and anyone with a little knowledge of tools can make it for himself.



By arranging on an upright board a double series of binding posts for the attachment of the electrodes, and also by the use of a number of copper disks in the base of the stand for direct con-

tact when platinum dishes are used as electrodes, the capacity for continuous and manifold work is great. The stand is provided with a cut-off switch to control the current, and all the wires are hermetically sealed within the stand, thus protecting them from vapors, acids, etc.

The stand, as illustrated here, consists of a base fifteen inches long, six inches wide, and about seven-eighths of an inch thick. To one of the long edges is fastened an upright piece thirteen inches long, six inches wide, and seven-eighths of an inch thick, forming the back ; and above this is the top, a piece of the same length and thickness, but only three inches wide, which projects horizontally over the back on both sides.

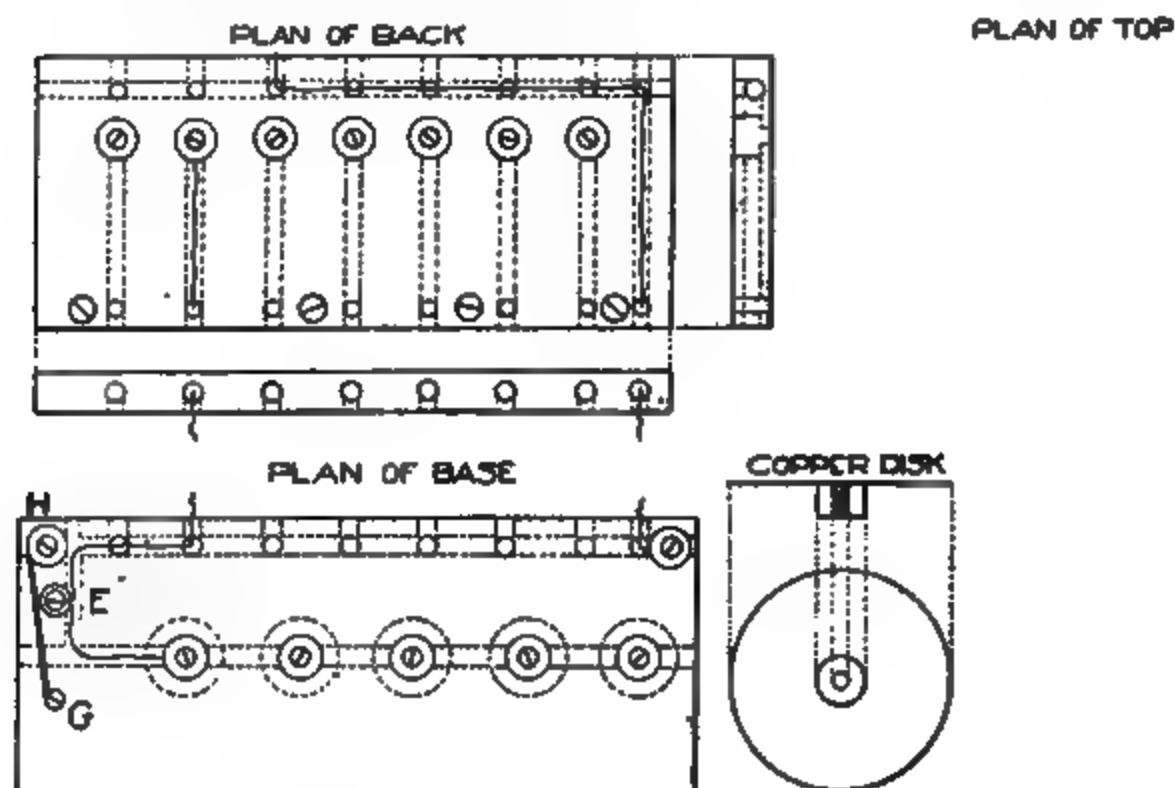
On the rear corners of the base are the two binding posts for connection with the battery wires, one of which binding posts is in connection with all the positive electrodes, and the other is in connection by means of the switch with all the negative electrodes. In the middle of the base are set the copper disks, which are of thin copper, one and three-fourths inches in diameter, and may be of any suitable number, depending on the size of the base. To one side of the copper disk is soldered a small piece of brass rod tapped with a screw thread, as is represented in the diagram. Hence it is only necessary to sink a hollow in the top of the base, so that the disk shall lie flat on the surface, and it can be readily attached in the same manner as a binding post.

At one end of the base is the cut-off switch, which is quite essential in such a stand, as it is desirable to interrupt the current while attaching or removing a solution for electrolysis. On the back of the stand at about two-thirds of its height, is a horizontal row of binding posts ; and on the front edge of the top is another row of binding posts exactly corresponding to those below them in number and position. It is well to have as many pairs of binding posts as there are disks in the base of the stand.

Small tunnels, less than one-third inch in diameter, are bored through the various parts of the stand to contain the necessary wires. The arrangement of the wires will be readily seen from the accompanying diagrams, which show the tunnels, binding posts, and copper disks, and also the small holes at the tunnel intersections for facility in wiring. In the plan of the base, G is the switch-pivot, and is in direct connection with the main bind-

ing post H, while the switch makes and breaks contact at E with the cathodes and the copper disks.

The wire used for the different connections is insulated copper wire, No. 23, though that is entirely a matter of choice, but it should not be too thick or it will be found difficult to pass it through the tunnel connections. When the wires are all in and the connections completed, all openings to the tunnels are



plugged up with paper and sealed with paraffin wax; the bases of the binding posts and disks are also filled in with wax.

The stand can easily be made in a day's work, as it only takes a short time to bore the tunnels and adjust the connections; inserting the wires is the slowest task, but when this is once well accomplished and the openings sealed up, the stand is good for a great many years' wear, as all connections are carefully protected from injury by handling or otherwise, and the only danger to guard against is the burning out of the wires by a very strong current.

In the plans given here, the binding posts on the top of the stand are intended to carry the anodes; and the binding posts on the back for the attachment of the cathodes. It will also be noticed that the copper disks are in connection as cathodes,

though of course this order can be reversed by changing the order of the battery wires at the two main binding posts.

A further accessory to the stand, not shown in the illustration, is a small pocket compass set in the base to serve as a galvanometer, to show whether or not the wires from the battery are attached to the stand in the right order. The compass is surrounded by at least two turns of wire connected with the main binding posts and controlled by a suitable switch to prevent a short circuit. It is only useful when the battery is at a distance or in another portion of the building, and the battery wires do not happen to be marked. Of course, it must be determined by experiment, in which direction the needle swings when the current is traversing the stand in the proper direction, and a little mark put on the glass of the compass to show this. I have constructed one stand with such a galvanometer. It is also well to mark the positive binding post on the base, and the set of binding posts for the anodes. This can be neatly done with a small piece of paper gummed to the board.

A stand of the size here illustrated, should not cost over five dollars, including the labor; it should be made of hard wood, and the binding posts should be "sunder posts."

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## A MODIFIED AIR-BATH.

BY F. P. VENABLE.

Received January 10, 1898.

THIS air-bath is a modification of the one devised by Habermann.<sup>1</sup> The modifications serve to give a wider application to his bath and a publication is made of them to draw the attention of American chemists to the advantages of Habermann's idea rather than to make any claim for special originality in them.

The cut will make the construction and the use of the bath clear. A glass bell jar is provided with a knob for handling and three tubulures. One of these is for the introduction of a thermometer. The remaining tubulure on the top serves as a vent for gases and the one in the side provides for an air-current. Either or both of them may be closed with stoppers if it is so desired.

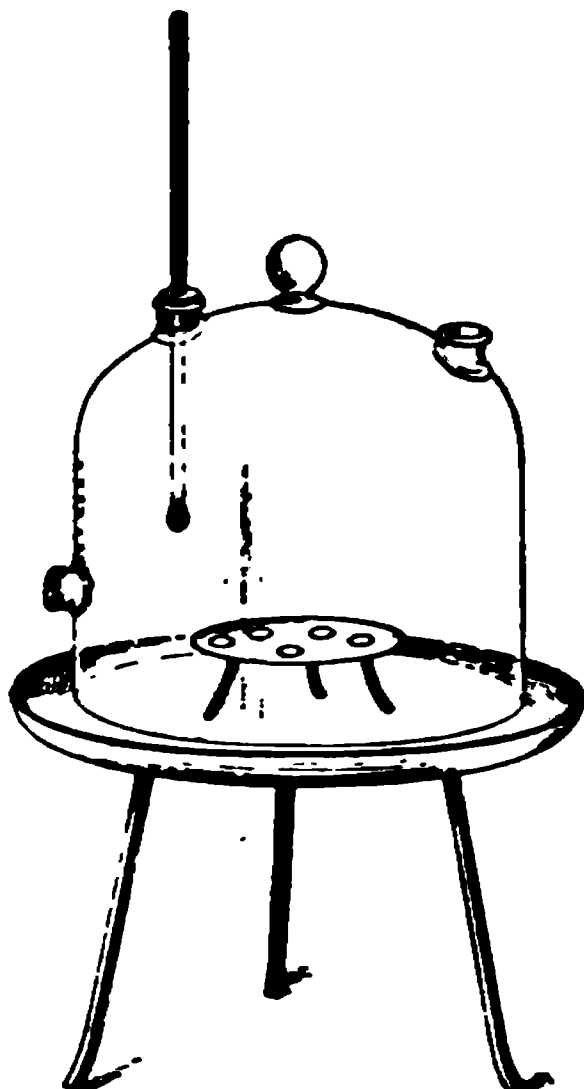
<sup>1</sup> *Ztschr. angew. Chem.*, 1897, 202.

This bell jar may be placed on the sand of a bath or better upon a ring of asbestos board on a sheet-iron pan or upon an iron plate. The object to be heated may be placed upon a tripod—a triangle or such a porcelain support, with perforations for crucibles, etc., as is frequently used in desiccators.

The advantages over the ordinary copper air-bath are :

1. Cheapness. A bell jar of ten inches diameter costs less than a third as much as the copper bath of the same dimensions.

2. Cleanliness. There is no corrosion from acid fumes. Incrustations upon the sides and roof of the jar are easily seen and removed so that there is no risk of their falling back into the



dishes or casseroles. It will then be especially useful for the drying down of acid solutions in the separation of silica.

3. The operation of drying can be watched.

4. The only part requiring renewal is the iron pan or plate and either one of these is very cheap. The burning out of the copper bottom of the ordinary air-bath is of distressingly frequent occurrence.

5. Any warm plate may, by this bell jar, be turned into a drying-bath in which the temperature can be watched and

regulated by increasing the thickness of the asbestos board or by other means.

I am strongly convinced of the wide application and general usefulness of this modified drying apparatus.

UNIVERSITY OF NORTH CAROLINA.

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CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, No. 8.

**SOME PROPERTIES OF ZIRCONIUM DIOXIDE.**

BY F. P. VENABLE AND A. W. BELDEN.

Received February 14, 1898.

**T**HERE are so many misstatements as to the properties of zirconia in the literature of chemistry that we think it well to publish the results of our study of this body.

1. *Specific Gravity*.—The following values have been given: 4.30 (Berzelius), 4.90 (Berlin), 5.50 (Sjögren), and 5.45 (Hermann). Our determinations were made with quite pure material and yielded as a mean 5.489.

2. *Solubility*.—The strongly ignited zirconia is practically insoluble in all acids except hydrofluoric. In this it is readily soluble on heating. If soda is present along with the zirconia, as sodium zirconate, the mass is not dissolved, probably owing to the formation of sodium zirconium fluoride. The statement is frequently met with that zirconia is soluble in sulphuric acid. This is based upon observations of Berzelius and his directions are that the zirconia must be finely powdered and heated with a mixture of two parts sulphuric acid and one part water until the sulphuric acid volatilizes. Our experiments would show that it is quite insoluble in concentrated sulphuric acid and when the directions of Berzelius are followed out this dilute acid dissolves only 6.72 parts to the 1,000 parts of acid. Neither concentrated nor dilute hydrochloric acid nor nitric acid seem to have much action upon it.

Prolonged heating with sodium carbonate effects very little change in zirconia. It is only sparingly dissolved. Berzelius must have made use of a carbonate carrying some hydroxide in the experiments in which he speaks of dissolving the zirconia by means of sodium carbonate.

Again, half a gram of zirconia (finely powdered) was fused for nine hours with twenty grams of microcosmic salt.

The zirconia did not apparently enter into the fusion nor could the formation of crystals be observed as has been maintained. The same results were observed in a similar experiment with borax.

3. *Zirconium Hydroxide*.—The statement is made in Dammer's Handbook (1, 619) that of the two possible hydroxides only  $\text{ZrO}(\text{OH})_2$  is known, and that, further, numerous pyrohydrates are known whose contents of water lie between this and the anhydride. This is based upon the work of G. J. Bruch,<sup>1</sup> who described a meta-zirconic acid,  $\text{ZrO}(\text{OH})_2$ , prepared as a white, voluminous, almost gelatinous precipitate, by precipitating a solution of a salt of zirconium with ammonia.

In the following experiments this precipitate, gotten with ammonium hydroxide, was washed free of ammonia, then placed in a Gooch crucible and washed about twelve times with alcohol (ninety-five per cent). It was then washed with ether. After weighing the crucible it was heated strongly and the loss of water was 26.50 per cent. In a second experiment the zirconium hydroxide precipitate was pressed between filter-paper, placed in a Gooch crucible, and washed with petroleum ether until there was no further loss of weight. This washing was done in an atmosphere free from carbon dioxide. Afterwards the crucible was strongly heated. The loss of water was 26.19 per cent. A third experiment carried out in a similar manner yielded also 26.30 per cent. Other experiments gave losses of 25.97 per cent. and 27.21 per cent. The percentage of water in  $\text{Zr}(\text{OH})_4$  is 22.69. It would therefore seem that treatment with petroleum ether brought the precipitate very nearly down to the composition  $\text{Zr}(\text{OH})_4$ . In using alcohol and ether there seemed to be no definite limit to the removal of water and hence in several experiments final constant weights were not obtained. Two experiments gave respectively 11.11 and 9.45 per cent. of water. The percentage in  $\text{ZrO}(\text{OH})_2$  is 12.80.

A specific gravity determination of the hydroxide containing 25.97 per cent. of water gave 3.25.

4. *Solubility of the Hydroxide*.—The statement of Bruch, that this substance is soluble in 5,000 parts of water and turns litmus

<sup>1</sup> *Jahresber*, 1854, 729.



paper blue and turmeric paper orange-yellow is cited by several authors. This is manifestly an error. The alkaline reaction observed was doubtless due to the ammonia which it so persistently retains when ammonium hydroxide is used in the precipitation. Bailey and others have noted how prolonged the washings must be to free the hydroxide from ammonia. Experiments were carefully carried out to test this point but we failed to detect in the pure hydroxide any alkaline reaction or any appreciable solubility in pure water. Certainly it is less than the figure given by Bruch.

The solubility of the cold precipitated hydroxide in acids is as follows: It is very readily soluble in concentrated and dilute hydrochloric acid (which is the best solvent for it), in hydrofluoric acid, and in hydrobromic acid. It is very sparingly dissolved by hydriodic acid. Concentrated and dilute nitric acid dissolve it easily.

Among the organic acids it was found that oxalic acid was the best solvent, dissolving it nearly as well as the mineral acids. Saturated solutions of tartaric and citric acids dissolved less than 1 : 1,000 and glacial acetic acid also dissolved very little.

If the zirconium hydroxide is precipitated from a hot solution it is much less soluble in the dilute acids. Thus dilute hydrochloric or dilute nitric acid will dissolve only about 1 : 100 and dilute oxalic acid dissolves only about half as much. If the precipitate, however, stands for some days in contact with the acid it is dissolved to about the same extent as when precipitated cold.

As to the solubility in basic substances, ammonia (sp. gr. 0.90) does not seem to appreciably dissolve it, but when diluted (sp. gr. 0.96) there is dissolved about 1 : 10,000 parts of ammonia. Clarke<sup>1</sup> has shown the solubility in potassium hydroxide, and in sodium hydroxide to be as follows :

							Gram.
50	per	cent.	KOH	solution	dissolved	per cc. ....	0.00233
33	"	"	"	"	"	"	0.00097
25	"	"	"	"	"	"	0.00075
12	"	"	"	"	"	"	0.00009
33	"	"	NaOH	"	"	"	0.00245
25	"	"	"	"	"	"	0.0012
12	"	"	"	"	"	"	0.0005

<sup>1</sup> This Journal, 18, 434.

Certain salts of ammonia exert quite a solvent action. Thus a saturated ammonium carbonate solution will dissolve about 1 : 100, and a solution of ammonium tartrate rendered strongly ammoniacal has a somewhat smaller solvent action.

5. *Absorption of Carbon Dioxide.*—Zirconium hydroxide shows a decided tendency to absorb carbon dioxide. This may be observed on exposing the moist precipitate to the air or on prolonged heating at a low temperature ( $100^{\circ}$ – $150^{\circ}$ ) over an ordinary burner. Such a mass will gain very noticeably in weight. The extent of this absorption of carbon dioxide was tested as follows: About two grams of the moist hydroxide were placed in a porcelain boat in a tube and pure carbon dioxide passed over it for some twenty-five or thirty hours. At the end of this time the hydroxide had contracted into small, hard, horn-like particles and no further change was observable. Purified air was next passed over these particles for eighteen or twenty hours and the carbon dioxide coming off was caught in a barium hydroxide solution and determined. Then the particles were heated and the carbon dioxide was caught by a fresh solution of barium hydroxide. It was found that about one-third of the carbon dioxide which had been absorbed came off without heating. As no distinct point could be observed at which this carbon dioxide ceased coming off (no clear line of demarcation between that lost at ordinary temperatures and that lost on heating), no inferences were drawn and the carbon dioxide was all reported together. The percentages of carbon dioxide absorbed were 16.42, 5.72, and 7.05. These show a wide variation and can scarcely be taken as showing more than the fact that considerable amounts of the gas are absorbed with the formation of basic carbonates. The basic carbonate,  $\text{Zr}(\text{CO}_3)_2 \cdot 2\text{Zr}(\text{OH})_2$ , contains 16.68 per cent. of carbon dioxide, and  $\text{Zr}(\text{CO}_3)_2 \cdot 6\text{Zr}(\text{OH})_2$  contains 7.55 per cent., and  $\text{Zr}(\text{CO}_3)_2 \cdot 8\text{Zr}(\text{OH})_2$  contains 5.96 per cent.

This experiment was varied somewhat by suspending the zirconium hydroxide in water and passing carbon dioxide through the water. This gave 6.73 and 6.00 as the percentages of carbon dioxide absorbed in two separate trials.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 27.]

## AMMONIUM SELENIDE.

BY VICTOR LENHER AND EDGAR F. SMITH.

Received February 26, 1898.

BY bringing ammonia and hydrogen selenide together Bineau<sup>1</sup> claims to have prepared ammonium selenide. His product was a white, crystalline solid, which was readily decomposed by water in the presence of air. No mention occurs anywhere that this compound was ever obtained by crystallization from solution, hence it may be of interest to note that when prepared by the latter method it crystallizes in black, anhydrous, orthorhombic prisms. Peculiar conditions, however, seem necessary for its formation. Thus, in attempting to make ammonium selenomolybdate it was observed that when an ammoniacal solution of ammonium molybdate was saturated with hydrogen selenide gas a dark-red colored solution resulted, which yielded the black crystals of ammonium selenide upon careful evaporation. The solution contained five grams of ammonium molybdate in fifty cc. of water, to which twenty cc. of the strongest ammonia water had been added. The solution was saturated with hydrogen selenide gas. The resulting liquid, deep red in color, was concentrated in a vacuum over sulphuric acid. The final residue consisted of ammonium molybdate, metallic selenium, and well-defined, black, orthorhombic crystals. The latter were separated as completely as possible from the selenium, and extracted for several days with pure carbon disulphide. The crystalline mass, purified as far as possible in this manner, proved to be stable in the air, and dissolved readily in water to a dark-red colored solution. The latter, when freshly made, precipitated selenides from neutral or alkaline solutions of metallic salts. On exposure to the air, however, the solution of the salt suffered decomposition with the separation of black selenium. An excess of ammonia seems not to prevent the change.

The analysis gave as follows :

<sup>1</sup> *Ann. chim. phys.*, [2], 67, 227.

I. 0.3051 gram of substance gave 0.2137 gram selenium = 70.04 per cent. selenium.

II. 0.2031 gram of substance gave 0.1418 gram of selenium = 69.81 per cent. selenium.

*Ammonium.*

III. 0.2012 gram of substance gave 0.0603 gram of ammonium = 29.97 per cent. ammonium.

IV. 0.3036 gram of substance gave 0.0918 gram of ammonium = 30.24 per cent. ammonium.

The discrepancy between the found and calculated percentages is due to metallic selenium, which adhered to the ammonium selenide crystals. The salt was distilled with sodium hydroxide in determining the ammonium content. The liberated ammonia was absorbed by standard hydrochloric acid, the excess of the latter being titrated with standardized alkali.

In estimating the selenium a weighed quantity of the salt was dissolved in water containing a little sodium hydroxide. An excess of 'hydroxylamine' hydrochloride was added to this solution, from which the selenium separated completely after boiling several minutes. It was then transferred to a weighed Gooch filter, washed with water and dried at 105° for one hour. This method is far superior to the usual course of precipitating selenium by means of sulphurous acid.

The ammoniacal molybdate solution of the strength given in the preceding lines is the only solution from which the black crystals were obtained. Under these conditions the salt was always found, but with molybdate solutions of greater dilution or with such as contained arsenic acid or tungstic acid, evaporation showed nothing but metallic selenium.

UNIVERSITY OF PENNSYLVANIA.

<sup>1</sup> Privately communicated by Dr. H. F. Keller.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 28.]

## ELECTROLYTIC DETERMINATIONS.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received February 26, 1928.

### I. URANIUM.

SOME years ago one of us found that it was possible to completely precipitate uranium<sup>1</sup> from an acetate solution by means of the electric current. The deposit consisted of the hydrated protosquioxide of uranium, which was ignited and weighed as  $U_2O_5$ . Indeed, the procedure was adopted in the separation of uranium from the alkali metals when they were associated in certain rare minerals. It has frequently been used since that time by the author and its reliability has been fully confirmed. However, Heidenreich<sup>2</sup> evidently experienced some difficulty in obtaining satisfactory results, for he remarks: "Versuche, Uran aus seiner Acetatlösung quantitativ abzuscheiden führten zu keinem Ergebniss, selbst bei 50-stündiger Einwirkung des elektrischen Stromes." A method, requiring fifty hours, would scarcely be regarded as having value even if the final results were really good. The following experiments, however, show that not only can satisfactory results be obtained, but they furthermore leave little doubt as to the time-factor, which is of prime importance in all determinations.

A solution of uranium acetate was prepared, which contained 0.1185 gram of urano-uranic oxide ( $U_2O_5$ ) in ten cc. of the liquid. To the latter volume were added five-tenths cc. of concentrated acetic acid and the whole was then diluted to forty cc. with water, when it was electrolyzed with a current  $N. D_{40} = 0.18$  A.  $V = 3$ . The temperature of the liquid during the decomposition was  $70^\circ$  C. The uranium was completely precipitated in six hours. The filtrate or solution poured from the deposit showed no traces of uranium, when it was evaporated and the residue tested for that metal.

<sup>1</sup> *Am. Chem. J.*, 1, 329; Smith's *Electrochemical Analysis*, p. 94.

<sup>2</sup> *Ber. d. chem. Ges.*, 29, 1587.

## RESULTS.

$U_3O_8$ present in grams.	$U_3O_8$ found in grams.
0.1185	0.1187
0.1185	0.1184
0.1185	0.1182

## 2. CADMIUM.

Those interested in electrolysis will probably remember that the writers have at various times proposed methods and conditions not only for the electrolytic determination, of this metal, but also for its separation from the more frequent associates. So often have we ourselves carried out these separations that we were inclined to believe other chemists would meet with like success. Such, however, seems not to have been the case, for in a very recent issue of this Journal<sup>1</sup> we felt called upon to publish very carefully outlined conditions for the complete deposition of cadmium from acetic and nitric acid solutions in order to again confirm our early statements. Heidenreich<sup>2</sup> mentions that the separation of cadmium from solutions containing sodium phosphate and free phosphoric acid gave results which were "ebenfalls nicht quantitativ; die letzten Reste von Kadmium sind nicht zu entfernen, selbst wenn der Strom bis 1-Ampère verstärkt wird." We regret exceedingly that this chemist has met with so little success in his efforts to repeat our work, but as in former instances of disagreement we again present new experimental evidence showing that our original suggestions were undoubtedly correct.

To ten cc. of a cadmium sulphate solution, containing 0.1656 gram of metallic cadmium, were added an excess of disodium hydrogen phosphate (1.0358 sp. gr.) and one and one-half cc. of phosphoric acid (1.347 sp. gr.). The liquid was then diluted to 100 cc., heated to 50° C., and electrolyzed with a current  $N. D_{100} = 0.06$  A. Volt = 3. The precipitation was finished in seven hours. The metal deposits were bright and adherent. They did not show the slightest trace of sponginess. At the expiration of four hours the current was increased to  $N. D_{100} = 0.35$  A. Volt = 7. The acid liquid was siphoned out without the interruption of the current. The pole separation, during the

<sup>1</sup> This Journal, 19, 870.

<sup>2</sup> *Ber. d. chem. Ges.*, 29, 1587.

entire precipitation, equaled one and one-fourth inches. The cadmium was washed with hot water and then carefully dried. The filtrates were examined but did not reveal a trace of unprecipitated metal. This is a direct contradiction of Heidenreich's statement that "die letzten Reste von Kadmium sind nicht zu entfernen."

## RESULTS.

	Cadmium present in grams.	Cadmium found in grams.
I .....	0.1656	0.1654
	0.1656	0.1658
	0.1656	0.1657

UNIVERSITY OF PENNSYLVANIA.

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### PRELIMINARY REPORT OF THE COMMITTEE ON COAL ANALYSIS.

*To the President and Members of the American Chemical Society :*

At the Cleveland meeting of the American Chemical Society a Committee, consisting of W. F. Hillebrand, C. B. Dudley and W. A. Noyes, was appointed to consider the methods of proximate analysis of coal with a view to the adoption, if possible, of uniform methods for this country. After discussion among themselves, the committee have formulated the following outline of methods for analysis which they herewith submit, rather as a means of securing further information than as a final report. The committee very earnestly request all chemists interested in the matter, who may see this report, to send to the chairman of the committee a criticism of the methods proposed and a statement of any objections they see, and of any modifications which they think desirable.

Since the literature of the subject is widely scattered and much of it is not easily accessible, the committee request that all who have published papers bearing on the subject will, if possible, send to the committee reprints of such papers, or, if that cannot be done, a statement of where such papers can be found and the points covered.

Without the full and hearty cooperation of others the labors of the committee will be greatly increased and the conclusions finally arrived at will be less representative of general experience than it is desired they should be.

## METHODS OF ANALYSIS.

1. *Sampling*: At least five pounds of coal should be taken for the original sample, with care to secure pieces that represent the average. These should be broken up and quartered down to obtain the smaller sample which is to be reduced to a fine powder for analysis. The quartering and grinding should be carried out as rapidly as possible, and immediately after the original sample is taken, to prevent gain or loss of moisture. The powdered coal should be kept in a tightly stoppered tube or bottle till analyzed.

2. *Moisture*: Dry one gram of the coal in an open porcelain or platinum crucible at  $104^{\circ}$ – $107^{\circ}$  for one hour, best in a double-walled bath containing pure toluene. Cool in a desiccator and weigh covered.

*Question*: Has any one experience with other methods of drying? over sulphuric acid, *in vacuo*, in a current of air, in watch-glasses, or otherwise? Especially in this and other cases, the committee desire any comparative results which can be furnished.

The following comparison of the effect of drying one hour in a toluene bath, twenty hours *in vacuo* over sulphuric acid, and in air over sulphuric acid was made by Dr. Hillebrand.

	One hour in toluene bath.	20 hours <i>in vacuo</i> over $H_2SO_4$ .	In air over $H_2SO_4$ .		
			2 hrs.	48 hrs.	120 hrs.
Coal No. 1.....	2.85	3.60	2.87	3.15	3.39
“ .....	3.10	3.59	....	....	....
“ .....	3.23	3.57	....	....	...
“ .....	3.25	3.49	....	....	....
“ .....	3.24	....	....	....	....
“ .....	3.22	....	....	....	....
“ .....	3.27	....	....	....	....
Coal No. 2.....	1.84	2.08	1.77	....	2.00
“ .....	1.83	2.07	....	....	....
Coal No. 3.....	1.52	1.75	1.42	....	1.70
“ .....	1.51	1.73	....	....	....
Coal No. 4.....	1.01	1.04	1.05	....	1.18
“ .....	1.08	1.03	....	....	....
Coal No. 5.....	1.40	1.69	1.45	....	1.66
“ .....	1.41	1.67	....	....	.. .
“ .....	...	1.67	....	....	....
Coal No. 6.....	0.30	0.21	0.23	....	0.25
“ .....	0.34	0.28	....	....	...



These results seem to indicate that drying *in vacuo* gives higher and, probably, more correct results than drying at 105° for one hour.

The following experiments were carried out by Mr. W. E. Burk at the Rose Polytechnic Institute<sup>1</sup> for the purpose of determining whether volatile matter other than water is lost in drying bituminous coals. A hard glass tube was partly filled with copper oxide, partly jacketed with a glass sleeve so that a portion could be heated to 100° by a current of steam. The coal was weighed in an aluminum boat enclosed in a weighing tube, and was then heated to 100° for an hour in a current of dry air. The moisture and any volatile matters which were expelled were passed over the heated copper oxide and the water and carbon dioxide were absorbed as usual in calcium chloride and in potash bulbs. The results were as follows :

Weight of coal taken.	Loss in weight of coal at 100°	Water found in calcium chloride tube.	Per cent. of water in coal.	Per cent. of carbon found in potash bulbs.	Per cent. of excess of hydrogen found.
1.4217	0.1994	0.2014	14.00	0.048	0.016
1.1195	0.1596	0.1625	14.25	0.058	0.029
3.1079	0.2111	0.2113	6.78	0.022	0.001
3.2356	0.2152	0.2142	6.65	0.025	.....
2.9408	0.1967	0.1967	6.65	0.037	.....

The amount of moisture found was slightly higher than was found in the same coal by the usual method, perhaps because of the current of dry air over the coal. Since the loss of volatile matter other than water was always less than one-tenth per cent., it can safely be disregarded for most practical purposes, with coals of this class.

3. *Volatile Combustible Matter*.—Place one gram of fresh undried coal in a platinum crucible, weighing twenty to thirty grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom six to eight cm. above the top of the burner. The flame used should be twenty to twenty-five cm. high when burning free, and the determination made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find " Volatile Com-

<sup>1</sup> See Proceedings of the Indiana Academy of Sciences for 1896, p. 113.

bustible Matter," subtract the per cent. of moisture from the loss found here.

*Questions:* Should a larger portion be taken? Should the coal be heated more gradually at first? Should a blast be used? Can results be obtained by heating in a muffle, or in any other manner, which will agree with those obtained by this method?

The committee consider the determination as largely arbitrary, in any case, and believe that uniform results in the hands of different chemists will be best secured by making the conditions as simple as possible. The most serious objection to the method proposed appears to be the danger of mechanical loss at the commencement of the heating. It is believed, however, that the error from this source is less than would arise from any method which leaves the application of the heat to the judgment of the operator.

The committee especially desire to secure any analytical data which may be available to show the degree of concordance of results obtained by the same or different chemists. Also any comparison of analytical results with results of commercial coking.

4. *Ash.*—Burn the portion of coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter.

*Question:* Are carbonates likely to be present in the ash in such amount that heating over a blast would lessen the weight appreciably?

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of the ash and, since three atoms of oxygen replace four atoms of sulphur the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee is not now prepared to recommend such a correction.

5. *Fixed Carbon.*—This is found by subtracting the per cent. of ash from the per cent. of coke as found in paragraph 3.

6. *Sulphur*.—What methods are used? Eschka's, with sodium or potassium carbonate, fusion with sodium carbonate and potassium nitrate, Carius' or others? Any comparative results are especially desired.

7. The committee would recommend that the heating effect be calculated on the basis of the coal burned to carbon dioxide and vapor of water at  $100^{\circ}$  C., and be stated either in calories per kilogram or English heat units per pound. The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogram by 536 or the number of English heat units per pound by 965. In either case it expresses the theoretical number of kilograms or pounds of water converted into steam from and at  $100^{\circ}$  C. by one kilogram or pound of the coal.

A calculation of the results of twenty-one analyses, and determinations of heating effect with the bomb calorimeter, made with Indiana and Pittsburg bituminous coals, shows that the heating effect may be found in all cases examined, with a maximum error of two per cent., by the following rule:

Subtract from 100 the per cents. of moisture and ash and one-half the per cent. of sulphur, and multiply the remainder by 80.7. The product will be the heating effect of the coal burned to vapor of water, expressed in calories.

The committee will be glad of any data which will enable them to further test this factor and also of any data with regard to other methods of determining heating effect.

Persons interested in the subject of coal analysis are requested to send any communications which they may wish to make, to Prof. W. A. Noyes, Rose Polytechnic Institute, Terre Haute, Ind.

W. A. NOYES,  
C. B. DUDLEY,  
W. F. HILLEBRAND,  
*Committee.*

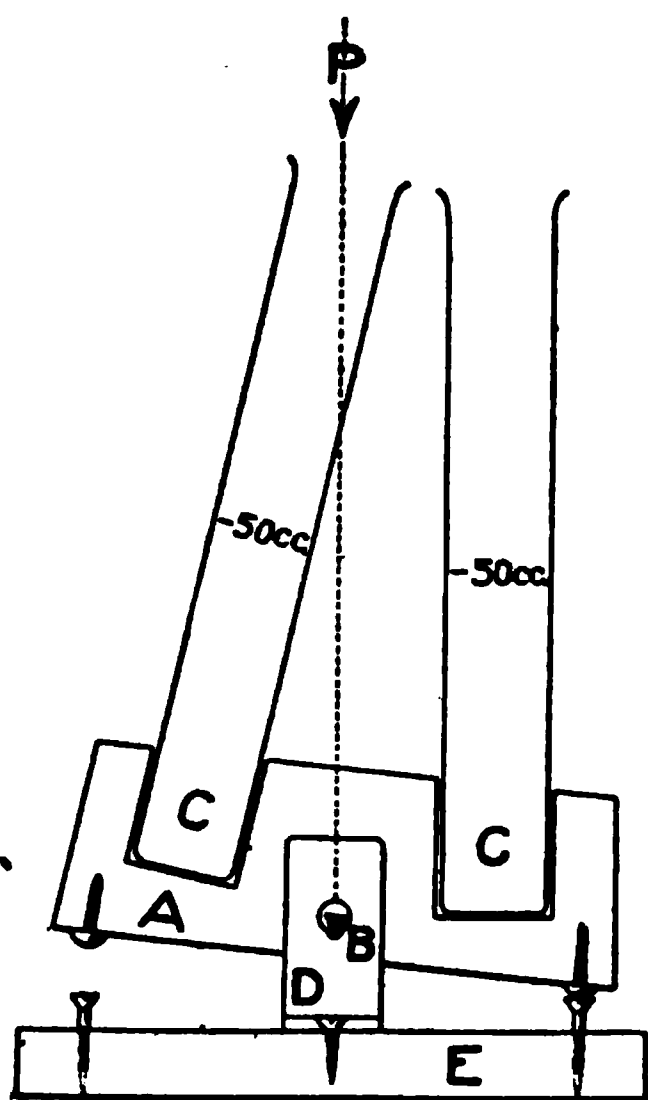
February 22, 1898.

# A COLLECTOR FOR DISTILLATION OF AMMONIA FROM WATER.

By F. P. DUNNINGTON.

Received February 4, 1898.

**I**N the familiar process of making a determination of free and albuminoid ammonia in water, the close attention which is demanded to change the receptacle as each of the several portions of fifty cc. is collected, is somewhat engrossing to anyone when conducting other analytical work. To avoid this embarrassment I have devised the following simple apparatus, which, for lack of a better name, is called a collector.



The figure presents a section of one-fourth size. From this the arrangement and working of the apparatus may be understood. It is made as follows :

In a block of dry poplar or other light wood, A,  $43 \times 53 \times 150$  mm., a hole of three mm. diameter is made at B for the pivot, and the large holes, CC, for Nessler tubes, are placed at the

same distance from the center of the block and equally inclined, as indicated. When the Nessler tubes are twenty-nine mm. in diameter, these holes should be about thirty-one mm. and be lined with a strip of woollen cloth to afford a snug fit for the tubes. The pivot B is a knife edge, made by grinding at its ends, a piece of a double three-inch saw file about fifty-five mm. long, and is merely hammered into the small hole cut for it. The knife edge is supported by a pair of plain two-inch angle irons (such as are kept in stock at a hardware store); in each of these, the hole in the upright limb is bored out and filed to the shape shown in the figure. These irons, D, are screwed to the wooden base, E,  $170 \times 170 \times 20$  mm.

The motion of the block, A, is checked by two round-head screws fastened into the under side of A, and by two flat-head wood screws partly screwed into the block E. By screwing the latter up or down you may adjust the apparatus so that when one tube is empty and the other is being filled, as soon as the latter collects fifty cc. of water, it topples over and immediately brings the other tube under the point P, to collect the distillate. While the second tube is being filled, you may hold the block A, remove the first tube and empty or replace it by another tube of same size and weight; when the second tube has collected fifty cc. it will topple over and again bring the mouth of the empty tube under P. The screw which serves to fasten each angle iron in place also passes through one end of a slip of thin sheet brass  $15 \times 30$  mm., the other end of which is bent up at right angles, so serving to keep the pivot from shifting to one side, but not binding upon it. This piece of brass is not shown in the figure, since it would cover the pivot end.

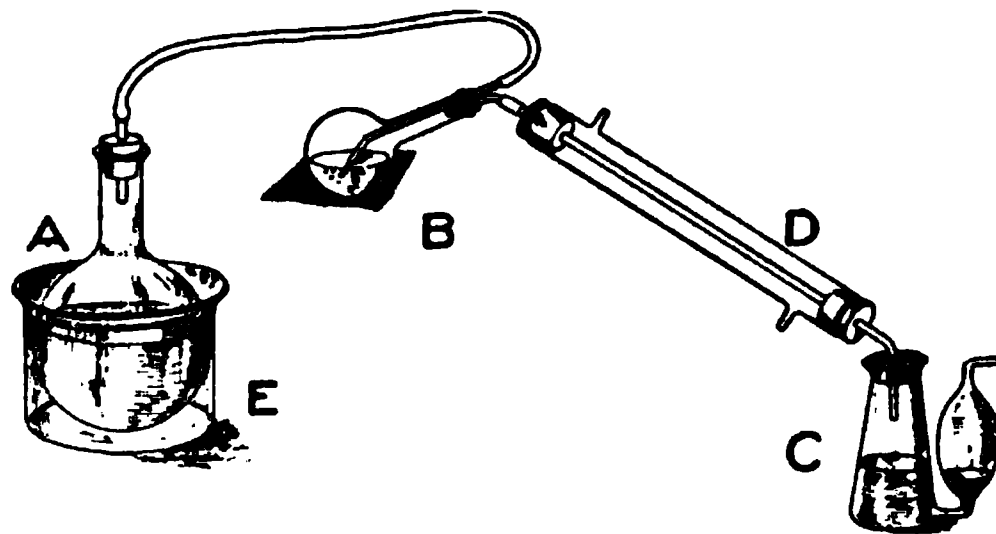
The Nessler tubes used are 29 mm. in diameter and 195 mm. long, and weigh 49 grams; should the tubes be heavier, it would be necessary to bore the hole for the pivot at a point a little higher up on the center line of the block A. It is easy to adjust this apparatus so that the amount required to topple the tubes will not vary as much as one-half cc. from the fifty cc.

## BORIC ACID DETERMINATION.<sup>1</sup>

BY THOMAS S. GLADDING.

Received February 7, 1898.

FOR the determination of boric acid I find the following method gives satisfactory results :



One gram of the substance in which the boric acid is to be determined is washed into flask B (150 cc. capacity), with a little ninety-five per cent. methyl alcohol. Five cc. of sirupy eighty-five per cent. phosphoric acid are added. Flask A is filled two-thirds full of ninety-five per cent. methyl alcohol and placed in the water-bath E. Flask B is now connected with the condenser D, and flask C placed in position to receive the distillate. Heat is now applied to the water-bath E and, when the methyl alcohol is boiling, flask A is connected to the tube which passes to the bottom of flask B. A current of methyl alcohol vapor is thus continually passing through the liquid in flask B, and carries over the boric acid. Heat is applied under flask B and so regulated that the liquid remains between fifteen and twenty-five cc.

The distillation is carried on in this way for about one-half hour, the distillate finally amounting to about 100 cc. A mixture of 40 cc. glycerine and 100 cc. water is now carefully neutralized, using phenolphthalein as an indicator, and then added to the distillate, which is then titrated with standard soda. The distillation must be continued until no more acid is obtained. Usually, it is complete in thirty minutes.

<sup>1</sup> Read before the New York Section, February 4, 1898.

A blank should be run using all the reagents, and any acidity found must be deducted from the final results.

The following results were obtained with borax and boric acid : One gram borax gave 36.57 per cent. boric acid, the theoretical per cent. being 36.65 per cent. ; one gram boric acid gave 99.9 per cent. boric acid.

A distillation of crystallized boracic acid, without the addition of phosphoric or other acid, was found to yield all the boric acid present. A similar distillation of borax was found to yield 19.50 per cent. boric acid out of a total of 36.65 per cent. present, or slightly more than fifty per cent. of the whole amount. This behavior may be useful in some analyses.

A gentle suction, by means of aspiration bottle, upon flask C, is desirable to avoid loss by possible leakage.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 29.]

## ACTION OF SULPHUR MONOCHLORIDE UPON MINERALS.

BY EDGAR F. SMITH.

Received March 7, 1898.

SULPHUR monochloride has frequently been applied in organic chemistry in the synthesis of various bodies, and the results obtained by the employment of this reagent have invariably had great attraction and interest for the investigator. There are, however, other directions in which the same reagent may be followed with equal interest ; *e. g.*, in the action upon the natural products furnished by the mineral world. To illustrate, mention may be made of the behavior of such substances as arsenopyrite, chalcopyrite, pyrite, and marcasite with the reagent in question. Finely divided arsenopyrite and sulphur monochloride were brought together in a glass tube. After slight agitation, action set in, accompanied by the evolution of much heat, and the almost complete decomposition of the mineral. The tube was then freed from air by the introduction of carbon dioxide. It was sealed and heated to about the boiling-point of the sulphur monochloride ( $139^{\circ}$ ) for a period of nine hours. On cooling, beautiful olive-green colored plates or scales separated. After their removal from the tube and separation from the adherent liquid they proved to be deliquescent and

readily soluble in water. Their aqueous solution tested with potassium ferrocyanide and silver nitrate showed the presence of iron in the ferric condition, and also of chlorine. In subsequent decompositions the crystals were filtered out, and washed with petroleum ether; then they were dissolved in water and the iron content determined quantitatively by means of stannous chloride. In this manner it was proved that 32.6 per cent. of iron was present in the ferric condition in arsenopyrite. This is certainly a confirmation of the work previously carried out in this direction on arsenopyrite by Starke, Shock, and Smith.<sup>1</sup>

The petroleum ether solution from the ferric chloride crystals was distilled, the product diluted with water, and tested with hydrogen sulphide, when the arsenic was precipitated. Its quantity was not estimated.

Chalcopyrite treated in a similar manner with sulphur monochloride, was completely decomposed, with the production of ferric and cupric chlorides. Marcasite and pyrite also gave beautiful crystallizations of iron chloride. The decompositions were in both instances complete and the total iron content determined. On the addition of sulphur monochloride to marcasite and pyrite no action was observed in the cold. With chalcopyrite and arsenopyrite the evolution of heat, as already mentioned, was very great, so that the vessel containing them could not be held in the hand. This difference in behavior evidently indicates a marked difference in the union of the elements concerned. In pyrite and marcasite we deal with iron and sulphur alone and with them there is an absence of marked reactivity, whereas in arsenopyrite and chalcopyrite we have substitution products in which there is perhaps a less intimate union of the sulphur than exists in the pyrite and marcasite. It may be observed here that Brown,<sup>2</sup> while working with marcasite, found that it contained its total iron in the ferrous condition, but when this same mineral was dissolved in sulphur monochloride it gave a mass of iron chloride crystals showing the presence of about forty-one per cent. of iron in the ferric state. This would mean that this reagent undoubtedly acts as an oxidant; that its power is in a large measure due to its chlorine content,

<sup>1</sup> This Journal, 19, 948.

<sup>2</sup> *Proc. Am. Phil. Soc.*, 33, 1894.



so that we may say of sulphur monochloride, it is "chlorine in disguise." This view of its action is corroborated by other decompositions which will be presented later. The experiments upon which the preceding statements are based were carried out by Mr. F. W. Moore.

The mineral stibnite dissolved immediately and completely in sulphur monochloride with a violent ebullition and the generation of much heat. When the solution cooled crystals separated. These were collected and heated with water, with the formation of antimony oxychloride. Much heat was also evolved when cinnabarite and sulphur monochloride were mixed. To effect complete decomposition the mixture was heated in a sealed tube. On cooling long needles were observed throughout the liquid. These proved to be mercuric chloride. Chalcocite was also completely decomposed, with the production of a crystalline powder, which on examination was found to be cupric chloride. This is additional evidence of the oxidizing character of the solvent employed, and explains the reason for the obtainment of so much ferric chloride when using marcasite, which contains its iron in the ferrous condition. Tetrahedrite, although of a complex nature, yields in the cold to the influence of the sulphur monochloride, and crystals of ferric chloride appeared in a very short time, although to effect the complete decomposition of the mineral it was necessary to heat it with the reagent to  $140^{\circ}$  C. Sphalerite was not attacked in the cold, and at  $150^{\circ}$  its decomposition was very slight, but at  $250^{\circ}$  C. complete solution occurred. On cooling, a mass of anhydrous zinc chloride separated. This was quickly collected and treated with water when it dissolved with a hissing noise. The zinc in solution equaled 67.5 per cent.

Galenite, furthermore, was not affected in the cold, but at  $250^{\circ}$  C. was changed completely to lead chloride. Finely divided molybdenite was not attacked in the cold, nor was it entirely broken up after heating to  $300^{\circ}$  C. Many of these experiments show that, where the sulphur estimation of a sulphide is not desired, this method of decomposing such minerals may be of use in analysis. This is particularly true in the case of tetrahedrite. Mr. C. S. Reeve was kind enough to conduct these experiments for me.

At my suggestion, Mr. E. W. Pierce brought pure, artificial arsenic trisulphide in contact with sulphur monochloride. A violent reaction set in, and much heat was liberated. On repeating the experiment at a temperature of  $0^{\circ}$ , the reaction took place slowly with the gradual solution of the metallic sulphide and the appearance of a slight residue of sulphur, which disappeared on the addition of more sulphur monochloride. Nothing separated when the liquid was further chilled. Arsenic sulphide was precipitated from the diluted solution on the addition of hydrogen sulphide. The minerals linnaeite  $(\text{Co}, \text{Ni})_3\text{S}_4$ , millerite  $(\text{NiS})$ , gersdorffite  $(\text{NiAsS})$ , and rammelsbergite  $(\text{NiAs})_2$ , were also fully decomposed by the monochloride on heating the mixture in sealed tubes to  $170^{\circ}$  C. Metallic chlorides were formed in all instances and separated from the cold solutions. Cobaltite  $(\text{CoAs})$ , smaltite  $(\text{Co}(\text{FeNi})\text{As}_2)$ , and ullmannite  $(\text{NiSbS})$ , in a finely divided condition, were dissolved by the sulphur monochloride when heated to  $180^{\circ}$  C. in a sealed tube. These observations were made by Mr. Jos. Cauffman, who also found that rutile in powdered form was decomposed almost completely by the same reagent, with the production of titanium tetrachloride. This behavior suggested heating the oxides of molybdenum, tungsten, tantalum, and columbium, as well as the minerals wolframite, scheelite, and columbite with the same reagent, when all were dissolved, and from the cold solutions beautiful crystalline bodies separated. Some of these have been analyzed, while others are yet under examination and will be discussed in a later communication. The indications are that the action of the sulphur monochloride in these substances is both oxidizing and substituting. Combinations of the metallic haloids with sulphur monochloride are not produced. In the case of the sulphides and sulpho salts which were investigated, quantitative determinations of the products were only made in a few instances, for there was no question as to the completeness of the decompositions, and the character of the resulting bodies. Upon considering the facts which are here presented, we recognize that with the sulphides of non-metals, for example stibnite, the action is violent, and the decomposition complete. This is also true of arsenopyrite where arsenic probably facilitates the transposition, whereas with marcasite, pyrite, sphalerite, galenite,

etc., the reaction is more sluggish. From an examination of the excess of sulphur monochloride in these different experiments it would seem that the original sulphur of the mineral is merely dissolved out, for upon evaporation it separates in large quantities.

UNIVERSITY OF PENNSYLVANIA.

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## THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.

BY FRANCIS G. BENEDICT AND R. S. NORRIS.

Received March 12, 1898.

THE methods for the determination of alcohol ordinarily in use are for the most part physical. By means of the pycnometer, vaporimeter, and ebullioscope, we are able to determine with reasonable accuracy the amount of alcohol present in alcoholic beverages and solutions, which seldom contain under one per cent. of ethyl alcohol. When, however, the exact estimation of smaller quantities is desired, these methods are unsatisfactory.

The numerous chemical methods for the determination of alcohol depend for the most part on the oxidizing action of potassium bichromate, chromic acid, or potassium permanganate. Only a small portion of the research on the oxidizing action of these compounds, has been done with reference to their oxidation of alcohol. This is partly explained by the previous existence of the physical methods of analysis above referred to and by the fact that while many organic compounds are completely and readily oxidized to carbon dioxide and water, alcohol is oxidized with great difficulty, the oxidation ceasing usually with the formation of acetic acid. The iodoform reaction and the blue coloration produced with a sulphuric acid solution of molybdic acid, furnish tests of the greatest delicacy, and for the most part investigators have been satisfied with a qualitative demonstration of the presence of alcohol when occurring in such small quantities as to preclude the use of the ordinary quantitative methods.

Bodländer<sup>1</sup>, pursuing an investigation similar to that for which the methods here reported were devised, *i. e.*, the estimation of

<sup>1</sup> *Pflüger's Archiv*, 32, 398.

the small quantities of alcohol eliminated in the urine and breath of man, used a standard solution of chromic acid in concentrated sulphuric acid and estimated the alcohol by determining the amount necessary to completely reduce a given volume of this solution. He states that the oxidation of alcohol is complete; *i. e.*, the products are carbon dioxide and water. Bourcart<sup>1</sup>, Heidenhain<sup>2</sup>, Freyer<sup>3</sup>, and Kuriloff<sup>4</sup> find on the other hand that the oxidation with chromic acid or potassium bichromate ceases with the formation of acetic acid. Rose<sup>5</sup> used potassium permanganate as the oxidizing agent, and states that the alcohol was completely oxidized to carbon dioxide and water by decinormal potassium permanganate in a solution that contained forty per cent. of sulphuric acid.

Bodländer's method was tried and found not to give entirely satisfactory results owing to the formation and escape of aldehyde, the amount formed varying with slight changes in the manipulation. On the addition of a dilute solution of alcohol to the concentrated sulphuric acid solution of chromic acid, the odor of aldehyde can be easily detected. Furthermore the end-point is rather difficult to determine.

Potassium permanganate, in the presence of strong sulphuric acid, was tried as an oxidizing agent. It was necessary to heat the solution in order to complete the oxidation, and under these conditions the potassium permanganate is decomposed in the absence of reducing agents. It is believed however, where only approximate results are required, that the conditions can be determined under which the oxidation is complete, while the decomposition of the potassium permanganate, other than that produced by the alcohol, is very slight. The method used was to mix a definite volume of decinormal permanganate with forty per cent. of its volume of concentrated sulphuric acid, in a glass-stoppered flask. To this mixture the solution of alcohol was added from a burette, in small quantities at a time, and thoroughly mixed with it by shaking. The excess of permanganate was then determined by titration against a standard solution of

<sup>1</sup> *Chem. Centrbl.*, 1890, 1, 547.

<sup>2</sup> *Ztschr. anal. Chem.*, 1893, 32, 360.

<sup>3</sup> *Chem. Ztg.*, 19, 1184; *Ztschr. anal. Chem.*, 1897, 36, 328.

<sup>4</sup> *Ber. d. chem. Ges.*, 30, 741.

<sup>5</sup> *Chem. Centrbl.*, 1888, 308.

ferrous ammonium sulphate. For certain purposes in the investigation it was necessary to determine the alcohol vapor contained in a current of air, and since it was found that the permanganate solution was reduced by simply passing the air of the room through it, this reagent could not be used.

As we were not successful in securing the accuracy desired with any of the methods tried, it became necessary to devise one which would give fairly close results for solutions containing as low as 0.01 per cent. of ethyl alcohol.

The method adopted depends on the oxidation of the alcohol by an excess of chromic acid in a concentrated sulphuric acid solution, and the determination of the excess of chromic acid by titration against ferrous ammonium sulphate solution, the endpoint being established by a few drops of standard permanganate solution. The reagents required for the determination are :

1. A solution of chromic acid in concentrated sulphuric acid.
2. A solution of ferrous ammonium sulphate.
3. An approximately decinormal solution of potassium permanganate.
4. A standard solution of alcohol in concentrated sulphuric acid.
5. Chemically pure, concentrated sulphuric acid.

The chromic acid solution is made by dissolving 2.2064 grams of chemically pure potassium bichromate in just enough distilled water to effect complete solution, and then making up to 500 cc. with concentrated sulphuric acid, care being taken not to let the temperature rise to over 100° C. This corresponds to a solution containing three grams of chromic anhydride in one liter. The reagent preserved in a glass-stoppered bottle is fairly stable.

For the ferrous ammonium sulphate (Mohr's salt) solution forty grams of the pure salt are dissolved in water and, after the addition of thirty cc. of concentrated sulphuric acid, the solution made up to a liter. Made in this way the solution is very stable, showing but slight changes on comparatively long standing.

The potassium permanganate solution is made by dissolving three and three-tenths grams of the crystallized salt in a liter of water.

The standard alcohol solution is practically a solution of ethyl

sulphuric acid in concentrated sulphuric acid. About two grams of five per cent. alcohol (see below) are weighed into a fifty cc. graduated flask and concentrated sulphuric acid added slowly, keeping the mixture cool to prevent any volatilization of alcohol by immersion in cold water. After five cc. of the acid have been added in this way the flask is filled to the fifty cc. mark and the solution mixed by pouring back and forth into a beaker.

The alcohol used in preparing the standard was one of the better grades of commercial alcohol. Its strength was determined with the admirable pycnometer described by Dr. Squibb.<sup>1</sup> This pycnometer readily gives the specific gravity of alcohol to the fifth or sixth decimal place. Ostwald's pycnometer,<sup>2</sup> which has the advantage of being much cheaper, was also found to give quite satisfactory results.

An accurate table for determining the per cent. of alcohol in solutions containing forty per cent. of absolute alcohol or over, from the specific gravity, is given by Dr. Squibb in his *Ephemeris*.<sup>3</sup> For solutions containing less than forty per cent. the table<sup>4</sup> used by the Association of Official Agricultural Chemists is to be recommended.

A practical difficulty arises in weighing out small quantities of strong alcohol owing to its volatility. It is therefore recommended that an approximately five per cent. solution be first made, from which small quantities can be correctly weighed without material loss. For preparing this solution the following method was found to be the most satisfactory: A glass-stoppered Shuster dropping bottle such as is ordinarily used to contain indicators, was weighed when dry and clean. After adding about the required quantity of alcohol its weight was again taken. The alcohol was poured into a previously tared flask, the last traces being removed by careful washing with distilled water. The solution was then made up to the desired weight, and the per cent. of absolute alcohol in it calculated.

It is of the utmost importance that the concentrated sulphuric

<sup>1</sup> This Journal, 19, 3.

<sup>2</sup> Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen, W. Ostwald, p. 110.

<sup>3</sup> *Ephemeris*, 2, 541.

<sup>4</sup> Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, p. 65.

acid used in these experiments be free from organic or other reducing matter.

To find the value of each solution in terms of the other, the ferrous ammonium sulphate is first titrated against the potassium permanganate. A measured volume of the chromic acid solution, generally ten or twenty cc., is then poured into 100–200 cc. of water, enough of the ferrous ammonium sulphate solution added to completely reduce it, and the excess of ferrous ammonium sulphate determined with the potassium permanganate. Twenty cc. of a chromic acid solution of the above strength oxidizes about seventeen cc. of the ferrous ammonium sulphate solution. Owing to the viscosity of the chromic acid solution it is necessary to adopt a definite method of delivery in order to obtain the same quantity each time. This result was secured by allowing the solution to run freely from an ordinary pipette made to deliver ten cc. Toward the end of the delivery the drops ceased quite suddenly to fall in quick succession and followed each other only at intervals of several seconds. The first "slow" drop was taken and the pipette removed immediately. This method apparently gave equal volumes of liquid.

The amount of chromic acid required to oxidize a given weight of alcohol, was determined by means of the standard solution of alcohol in concentrated sulphuric acid. Ten cc. of chromic acid solution were drawn off into a small flask, and a measured amount (about three cc.) of the standard solution of alcohol added from a burette.<sup>1</sup> The mixture was heated with constant agitation over a free flame to 98° C.<sup>2</sup> (a thermometer being held in the solution) and kept at about this temperature for five minutes. Under these conditions no aldehyde was formed. After cooling the solution it was poured into 200 cc. of water, ferrous ammonium sulphate added from a burette until the red color of the chromic acid had entirely disappeared, and the excess of ferrous ammonium sulphate titrated back with the potassium permanganate.

<sup>1</sup> Considerable time is required for the sulphuric acid solution to run down the sides of the burette. The readings should not, therefore, be made until it is ascertained that the meniscus is stationary.

<sup>2</sup> According to Cross and Bevan, *J. Chem. Soc.*, 53, 889, chromic acid in concentrated sulphuric acid solution gives off oxygen at 105° C. Numerous tests showed no decomposition of the chromic acid solution after five minutes' heating at 98° C.

The standard solution of alcohol used contained 237.6 mgms. of alcohol in 100 cc. In four titrations of this solution we obtained the following results :

	Alcohol solution.	Equivalent in ferrous ammonium sulphate solution.	Ferrous ammonium sulphate solution equivalent to one cc. of alcohol solution.
	cc.	cc.	cc.
I.	4.00	9.70	2.43
II.	4.95	12.00	2.42
III.	2.95	7.20	2.44
IV.	3.10	7.60	2.45
Average.....			2.43

Since a cubic centimeter of the alcohol solution contained 2.376 mgms. of alcohol, one cc. of the ferrous ammonium sulphate solution would be equivalent to 0.978 mgms. of alcohol. This factor was used in calculating the alcohol in the other solutions.

In order to test the accuracy of the determination, solutions of different strengths were made by the method used in preparing the standard solution.

The following results were obtained upon analysis :

	Weight of alcohol.		Volume of solution. cc.	Per cent. of alcohol.	
	Calculated. Mgms.	Found. Mgms.		Calculated. Per cent.	Found. Per cent.
I.	38.18	38.18	100	0.038	0.038
II.	30.63	30.05	50	0.071	0.070
III.	853.00	885.00	500	0.171	0.177
IV.	7.24	7.12	100	0.00724	0.00712
V.	11.01	11.23	50	0.02202	0.02246

An extremely dilute solution was made by diluting 12.34 mgms. of alcohol to 250 cc. The solution therefore contained 0.00494 per cent. of alcohol. The result obtained by titration was 0.00508 per cent., an error of about one ten-thousandth of one per cent. of alcohol.

In order to compare the accuracy of the method with that of Squibb's pycnometer for dilute solutions of alcohol, 31.44 grams of 90.61 per cent. alcohol was made up to 994.5 grams with water, giving a 2.865 per cent. solution. With Squibb's pycnometer the result was 2.95 per cent. when calculated from a table in the *Ephemeris*<sup>1</sup> and 2.84 per cent. when calculated from a more recent table.<sup>2</sup> By titration with the chromic acid the

<sup>1</sup> *Ephemeris*, 2, 563.  
<sup>2</sup> Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, 65.



strength was determined to be two and eight-tenths per cent.

As previously stated, one of the conditions to which the method must apply, was the determination of small quantities of alcohol in an air current.

Concentrated sulphuric acid according to our experiments removes alcohol from an air current even more completely than it does water. The apparatus with which this great affinity of sulphuric acid for alcohol was determined, consisted of a system arranged as follows: A current of air drawn by means of an ordinary Chapman filter-pump passed successively through a U-tube filled with cotton, a gas-washing cylinder containing concentrated sulphuric acid, a U-tube filled with soda-lime, a U-tube containing a known amount of alcohol, a cylinder similar to the first containing concentrated sulphuric acid, a 12-inch piece of combustion tubing containing a layer of copper oxide kept at a red heat by a four-tube burner, and a U-tube containing glass beads covered with about ten cc. of barium hydroxide solution, which in turn was connected by a rubber tube to the filter-pump. The tube with cotton was used to remove dust from the air. The sulphuric acid in the first cylinder removed the water, and the soda-lime the carbon dioxide. The air then passed over the alcohol and carried some of it into the sulphuric acid in the second cylinder. In case any of the alcohol was not absorbed by the sulphuric acid it would be burned by the hot copper oxide to form carbon dioxide, which would produce a precipitate in the barium hydroxide solution. Air was passed through the apparatus at the rate of 600 cc.<sup>1</sup> a minute.

In an experiment in which about nine-tenths gram of nineteen per cent. alcohol evaporated in nine hours, no barium carbonate was formed. In two other experiments in which half that quantity of alcohol was used it was also completely absorbed by the

<sup>1</sup> That it is possible to remove the alcohol quite completely from a current of air passing at a much more rapid rate than this, was subsequently demonstrated with a slightly modified apparatus. Owing to the fact that a rapid air current caused the combustion of the rubber stopper in the end of the short tube containing the copper oxide, by the hot air drawn against it, a tube thirty inches long was used and heated only at one end. The barium hydroxide U-tube in the apparatus above described, also was not very satisfactory for rapid currents of air, and was therefore replaced by a gas-washing cylinder containing about twenty cc. of barium hydroxide solution. A current of air containing alcohol vapor drawn through this apparatus at the rate of 2100 cc. a minute, produced only a slight turbidity in the barium hydroxide solution in the course of fifteen minutes. When the cylinder containing sulphuric acid was removed from the system, however, a heavy precipitate was instantly formed.

sulphuric acid. Forty cc. of concentrated sulphuric acid were used in each case.

Four solutions were prepared by this method and the alcohol determined by titration. The results obtained were as follows:

	Alcohol absorbed Mgms.	Alcohol determined Mgms.
I.	96.77	95.05
II.	90.37	89.56
III.	11.62	11.50
IV.	13.5	14.4

Two experiments were made to determine how much alcohol a given volume of concentrated sulphuric acid can completely remove from a current of air. In the U-tube immediately preceding the acid ninety per cent. alcohol was placed and its evaporation was facilitated by a loose roll of filter-paper in the limb of the tube next to the acid. Air was drawn through this apparatus for fifteen hours at the usual rate before a distinct appearance of barium carbonate precipitate occurred. The coating of the carbonate on the sides of the barium hydroxide tube was, at the end of this period, less in amount than that produced by the combustion of a milligram of alcohol. During the period approximately forty cc. of alcohol was evaporated. The sulphuric acid solution measured about ninety cc. and had a brownish-red color and a faint, pleasant, ethereal odor. It was made up to 100 cc. with concentrated sulphuric acid and five-tenths cc. measured out and made up to fifty cc. with more acid. This solution was titrated with the chromic acid solution and found to contain 3.43 mgms. of alcohol in each cubic centimeter. Accordingly the fifty cc. of concentrated sulphuric acid used in the first experiment had absorbed 34.3 grams of alcohol.

In the second experiment only thirty cc. of sulphuric acid were used, and the alcohol was made to evaporate more rapidly. About twenty cc. of ninety per cent. alcohol were volatilized in eight hours. In the beginning of the experiment the rapid absorption of the alcohol by the sulphuric acid caused an appreciable rise in the temperature. The sulphuric acid solution was diluted as in the first experiment, and the alcohol determined to be 1.72 mgms. in each cubic centimeter. The thirty cc. of sulphuric acid had therefore absorbed 17.2 grams of alcohol.

For the determinations of alcohol in dilute solutions we have found the following method the most satisfactory. Having prepared the standard solutions above described and determined the value of each in terms of the others, the strength of the unknown solution of alcohol is first determined roughly by means of an ordinary pycnometer.

If the solution contains more than one per cent. of alcohol, weigh out accurately such a quantity as will contain about one-tenth gram of absolute alcohol into a fifty cc. graduated flask and add ten cc. concentrated sulphuric acid carefully, the flask being immersed in cold water and continuously shaken to prevent a rise in temperature. The solution is then made up to the fifty-cc. mark with concentrated sulphuric acid, thoroughly mixed, transferred to a burette and about five cc. drawn off into a small flask. Twenty cc. of the chromic acid solution are then added, using the same precautions for the delivery of the solution as when it was standardized. The contents of the flask are heated to  $98^{\circ}\text{C}$  (a thermometer being immersed in the liquid) and kept at this temperature for five minutes. The solution is then cooled down to the room temperature, poured into 200 cc. of distilled water and ferrous ammonium sulphate added from a burette until the excess of chromic acid is completely reduced, as is indicated by the disappearance of the red color. The excess of ferrous ammonium sulphate is then determined with the standard potassium permanganate. It is best to add a single drop of the potassium permanganate solution at first in order to be sure that there is an excess of ferrous ammonium sulphate present. The amount of alcohol per cubic centimeter is calculated thus: The amount of ferrous ammonium sulphate solution used (after making allowance for the permanganate required for the back titration) is subtracted from the number of cubic centimeters of ferrous ammonium sulphate equivalent to the chromic acid solution used, and the result divided by the number of cubic centimeters of the alcohol solution taken. This gives the volume of ferrous ammonium sulphate solution in cubic centimeters equivalent in reducing power to one cc. of the solution of alcohol. Multiplying this by the factor previously determined, which expresses the number of milligrams of alcohol equivalent to one cc. of ferrous ammo-

nium sulphate, gives the weight of alcohol in one cc. of the sulphuric acid solution.

If the original solution contains one per cent. or less of alcohol, draw 0.5 cc. into a 100-cc. flask and add about five cc. of concentrated sulphuric acid, keeping the liquid cool during the addition. Add ten cc. of the chromic acid solution and proceed as above. This determination will serve to indicate approximately how much alcohol there is in the solution so that in subsequent titrations enough of it can be taken to reduce from sixty to eighty per cent. of the chromic acid. The amount of sulphuric acid added in each case should be equal to about twice the volume of the solution of alcohol used.

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## ALUMINUM USED AS AN ELECTRODE.

BY GEORGE J. HOUGH.

Received February 3, 1898.

AS the result of a number of experiments in quantitative chemical analysis by electrolysis, I take pleasure in stating that aluminum can be used as a substitute for platinum, as an electrode, though only to a limited extent.

It can be used as the cathode with nitric acid solutions, and apparently is not affected by the electrolytic action. Theoretically, it should not be affected as a cathode during the electrolysis, any more than the metals are affected which are precipitated there.

It is unserviceable, however, as an anode, as it is readily oxidized at that pole and dissolved in the acid solution. Neither can it be used in sulphate or chloride solutions, as the free acid readily attacks it; but if the sulphate or chloride solution be changed to the double oxalate of potassium or ammonium, as recommended by Classen, the aluminum cathode is not affected. This aluminum cathode can also be used with cyanide solutions, for although aluminum is readily attacked by hot solutions of potassium cyanide or oxalate, it apparently is not affected in the cold, even under electrolytic action.

The idea of substituting aluminum for platinum as an electrode, was suggested to me by the fact that aluminum is not

affected by hot or cold nitric acid, and metals plated on it could be readily dissolved off without injuring the electrode ; but as the best aluminum on the market is not quite pure, there is a possibility in time of a slight loss in weight. Even with this drawback, however, aluminum cathodes will be serviceable for ordinary commercial analysis, especially copper analysis, in which I think they would find their greatest field of usefulness.

It has been suggested to me that aluminum, heavily plated with platinum, might be made to serve as an anode ; but of this I am somewhat doubtful, as I have not yet had opportunity to try it.

This substitution of aluminum for platinum I make simply as a suggestion, for my experiments have not been numerous enough or minute enough to announce it as a scientific improvement, except in the case of copper analysis.

But should it prove to be sufficiently adapted to the purpose which I have designated, it has two great advantages : first, as compared with platinum it is very much lighter, and its use would reduce the liability to error in the weight of the deposited metal, which is small as compared with the weight of the electrode ; second, it is vastly cheaper than platinum, costing only one-sixtieth as much in the manufactured condition.

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### NOTE ON LIQUID PHOSPHORUS.

By F. P. VENABLE AND A. W. BELDEN.

Received February 14, 1898.

IN 1875 Hourton and Thompson<sup>1</sup> reported the formation of a peculiar modification of phosphorus formed on boiling ordinary phosphorus for five minutes with a strong solution of potash. The alkaline solution was poured off and the liquid phosphorus washed. It is said to remain liquid for months and solidifies only on cooling to  $+3.3^{\circ}$ . It is further reported as not oxidizing in the air nor giving off light in the dark. On becoming solid it forms ordinary wax-like phosphorus and a second variety of crystalline phosphorus.

These singular statements are cited in Dammer's "Handbuch der anorganischen Chemie" and the chemical literature available to us has been searched in vain for any further mention of this

<sup>1</sup> *Arch. d. Pharm.*, (3), 6, 49.

strange variety of phosphorus. It has therefore seemed advisable to give a brief notice of some experiments in which it was attempted to form this liquid phosphorus.

Five grams of fresh wax phosphorus were placed in a flask with 80 cc. of a saturated solution of potassium hydroxide and boiled for five minutes in a neutral atmosphere (nitrogen was used). This was washed with water at 19° and on the second washing the phosphorus solidified. If the alkaline solution was poured off directly, the phosphorus caught fire, hence it was usually poured off to small bulk, diluted with water, and again poured off and so on until the phosphorus was washed. In every experiment performed the phosphorus solidified after the second or third washing. The amount of phosphorus, the time of boiling (three, five, ten, and fifteen minutes), and the strength of the potassium hydroxide solution (saturated to ten per cent. solution), were each varied without securing the liquid phosphorus.

It is, however, true that the phosphorus becomes liquid on heating under the alkaline solution and, if left covered with the same, stays liquid a long time, solidifying only when strongly cooled. It seems to give off occasional bubbles of gas during this standing and is probably being slowly changed into phosphine at ordinary temperatures. We are quite at a loss to know how the authors mentioned above secured their liquid phosphorus and how it could prove unalterable in the air. In all of our experiments it was peculiarly inflammable.

UNIVERSITY OF NORTH CAROLINA.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNITED STATES DEPARTMENT OF AGRICULTURE, No. 32.]

**CALORIES OF COMBUSTION IN OXYGEN OF CEREALS  
AND CEREAL PRODUCTS, CALCULATED FROM  
ANALYTICAL DATA.<sup>1</sup>**

BY H. W. WILEY AND W. D. BIGELOW.

Received March 10, 1898.

**PRINCIPLES INVOLVED.**

**T**HE calculation of the heat of combustion of food products is now quite generally practiced in analytical determinations. The development of the methods of burning in com-

<sup>1</sup> Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.

pressed oxygen as proposed by Berthelot and Veille, has made it possible to use this process for ordinary purposes, and with a fair degree of accuracy. The data obtained by combustion in oxygen become, therefore, a check upon ordinary analytical determinations, as well as an additional means of measuring the dietetic value of foods. When the data obtained on combustion are to be used in analytical methods it is necessary to compare them directly with the data calculated from chemical analysis. A large number of difficulties arises in connection with this calculation on account of the number of combustible substances present in the cereals and their products. We have three great classes of bodies in cereals, namely, carbohydrates, proteids, and oils. In addition to these, however, there are many others which are oxidizable, and which yield heat in the process, among them amid compounds of nitrogen, organic acids, lecithins, and coloring-matters. These last named, it is true, exist in minute quantities, but the combustion of the whole of them is attended with a considerable evolution of heat, which must not be lost sight of in exact comparisons. In addition to this, the groups of like matters which form the chief part of cereals and cereal products are composed of several substances. In the carbohydrates are found many different classes whose heats of combustion vary largely. For instance, there is a wide difference between the heat of combustion of a gram of pentosans and a gram of starch, and midway between these lies the number representing the heat of combustion of sucrose. The different vegetable oils vary greatly in their calorific power, and these differences must be taken into consideration in the calculations. In respect of the heats of combustion of the vegetable proteids, but little is known, and we have not yet isolated sufficient quantities of the different proteids to determine the heat of combustion of each one directly. This part of the subject will be investigated further. The results of the actual determinations, however, show that the average number of small calories per gram of vegetable proteids evolved in burning in oxygen is not far from 5900.

#### CALORIES OF THE CARBOHYDRATES.

The details of the processes employed for cereals and cereal

products will be considered by classes, beginning with the carbohydrate group.

The magnitude of the calorimetric equivalents of the carbohydrates and their derivatives shows in general regular and expected variations, depending on their constitution and molecular configuration. Isomeric bodies show similar but not always identical heats of combustion. For the three groups of carbohydrates, presented by the formulas  $C_6H_{12}O_6$ ,  $C_{12}H_{22}O_{11}$ , and  $(C_6H_{10}O_5)_n$ , respectively, the heats of combustion at constant volume for one gram-molecule are about 673, 1351, and 678 calories respectively. In derivatives of the carbohydrates the heat value decreases in general with the increase of the hydrogen and oxygen atoms with reference to the carbon atoms, but this rule is not rigidly applicable, and does not permit a sure judgment in respect of heat value based on a knowledge of chemical composition alone. The heat value of the pentoses is generally less than that of the hexoses, and of the hexoses the more condensed forms, as for instance the disaccharids and polysaccharids, like starch, have a higher heat value than the simpler forms like dextrose. In round numbers the heat value of the pentoses (arabinose, xylose) and of lactose (crystallized), dextrose and fructose, is 3750; of sucrose, maltose, and lactose (anhydrous) 3950; and of starch and cellulose 4200 calories per gram. In computing the heat value of a mixed carbohydrate body from analytical data, it is therefore necessary to know approximately the relative quantities of these typical constituents. If, for instance, in a cereal (ground wheat) containing seventy-four per cent. of carbohydrates it is desired to calculate the heat value accurately, it is first necessary to distribute the total carbohydrates into groups. Suppose it be found on analysis that the total carbohydrates are composed of the following quantities:

	Per cent.
Pentosans .....	4.5
Cellulose (soluble and insoluble fiber) .....	4.5
Sugar (sucrose) .....	1.0
Starch .....	64.0

The heat value of the pentosans is about fifty calories greater than for the pentoses, and the factor for pentosans is therefore  $3750 + 50 = 3800$ . Cellulose and starch have practically the



same heat value, and the factor for these in round numbers is 4200. The sugar is chiefly sucrose, and the factor for this is 3950. The above numbers give the necessary data for the computation given below.

COMPUTED CARBOHYDRATE CALORIES FOR ONE GRAM OF A CEREAL  
FLOUR CONTAINING 74 PER CENT. OF CARBOHYDRATES.

	Gram.
Total weight of carbohydrates .....	0.740
Weight of pentosans, etc.....	0.045
Weight of starch, cellulose, etc.....	0.685
Weight of sucrose, etc.....	0.010

Then :

	calories.
$0.045 \times 3800 =$	171.0
$0.685 \times 4200 =$	2877.0
$0.010 \times 3950 =$	39.5
Sum	3087.5

CALORIES OF COMBUSTION OF VEGETABLE PROTEIN.

In respect of the heat of combustion of the vegetable proteid matters, it may be said that even greater variations are noticed than with the glycerids and carbohydrates; for instance, the calories obtained by the combustion of a gram of gluten, as ascertained by Berthelot, are represented by the number 5990.3. The mean number of calories per gram of the proteids in general is stated by Stohmann to be 5730.8. The calorimetric numbers for hordein, edestin, leucosin, zein, myosin, vitelin, gliadin, glutenin, and the other minor proteid bodies occurring in the cereals, have not been determined. Moreover, it must be remembered that the cereals contain a certain proportion of amid nitrogenous bodies, the heat values of which are considerably less than those of the pure proteids. It is a question, therefore, of considerable difficulty to select a factor which represents the proper number for computing its fuel value from the total nitrogen present in a cereal. In the "Principles and Practice of Agricultural Analysis", III, 559, the factor 5500 calories per gram is proposed as a suitable one for use with the proteids. This factor is probably too low for estimating the heat produced by the combustion of cereal protein in oxygen. Before the proteids are absorbed into the body and oxidized or distributed as con-

stituents of the tissues they are converted in the digestive organs into soluble forms, to which the general term peptones has been applied. The heat of combustion of peptones is decidedly less than that of the ordinary proteids, being represented by a factor 5300 calories per gram. The number given above, therefore, *viz.*, 5500 calories per gram, is about a mean to be used in calculating the calories of combustion of peptones and proteids. For the actual calculation of heats of combustion in oxygen of proteid matter of cereals to be compared with the heats of combustion obtained in the calorimeter, the factor 5900 is proposed as the one most nearly correct, in so far as our present knowledge is concerned.

We have made efforts to secure sufficient quantities of the pure proteids present in the different cereals to determine directly their calorific power. Owing to the difficulty of preparing these proteids in the large quantities sufficient for the work we have not yet succeeded in our object. We will, however, continue this work and either obtain the samples from others or, if unable to do this, prepare them ourselves, in order that the special factor for each cereal may be determined experimentally. In the absence of these special determinations we have only the recourse of making use of the factor which seems to be nearest the proper one for all; namely, 5900 calories for each gram of vegetable protein present in the cereal.

If all the nitrogen in a cereal product be calculated as proteid matter, the factor to be used in calculating the calories of combustion must be less than 5900. The reason for this is that a small part of the nitrogen present is in a non-proteid form, existing as compounds distinctly less calorific than protein matters. Only an approximate factor can be proposed for this calculation. It is best to determine the non-proteid nitrogen and then use the factor 5900 for the residual proteids. The nitrogen as amids in this case, in so far as its fuel value is concerned, is to be calculated by a different factor. Asparagin may be selected as a representative vegetable amid, and the calories corresponding to one gram of asparagin are represented by the number 3400. Asparagin contains 22.7 per cent. of nitrogen, and in order to convert amid nitrogen to asparagin its percentage is multiplied by 4.05. These data afford the basis of a

rational computation of heat values of the nitrogenous constituents of cereals.

*Example.*—The sample of wheat flour before mentioned contains 2.00 per cent. of nitrogen, of which 0.12 per cent. is of an amid nature. The proteids in the sample are calculated as follows :

$$1.88 \times 5.70 = 10.71 \text{ per cent.}$$

The amid bodies, as asparagin, are found from the following equation :

$$0.12 \times 4.05 = 0.48 \text{ per cent.}$$

In one gram of substance the calories of combustion are calculated as follows :

	calories.
0.1071 gram proteids $\times$ 5900	= 631.9
0.0048 " asparagin $\times$ 3400	= 16.3
	<hr/>

Total calories due to nitrogen compounds, 648.2

#### CALORIES OF COMBUSTION OF CEREAL OILS.

In order to secure a basis for rational work, the oils of the cereals were extracted and purified as carefully as possible by the usual methods. Three of these oils have already been subjected to combustion, while the process of the purification of the others is still going on. The oils which have been burned gave the following calories per gram: Wheat oil, 9359; rye oil, 9322; Indian corn oil, 9280. For the nearest round numbers the factor for wheat oil would be 9350, and for rye and Indian corn 9300.

In making calculations from analytical data, however, the ether extract does not represent a pure oil, but all the other bodies in the cereal which are soluble in ether. It is therefore deemed desirable to determine the calorific power of the ether extract, obtained according to the methods of the official agricultural chemists. For this purpose a considerable quantity of the ether extract of wheat, oats, barley, and rye was prepared, and the combustion of this extract was made directly. The results per gram of ether extract for the several cereals mentioned are as follows: Wheat, 9070; oats, 8927; barley, 9070; and rye, 9196 calories. The nearest round numbers for these bodies would therefore be wheat, 9100; oats, 8950; barley, 9100; and rye, 9200.

In the extraction of cereals with ether it should not be forgotten that a portion of the fatty matter is not brought into solution.

Especially is this true of the lecithins. In view of this fact, it is a matter of question whether it might not be advisable, with the present light on the subject, to multiply the ether extract by the round number 9300 rather than by the number corresponding to the calorific power of the ether extract itself as given above. With the exception of oats and Indian corn, the difference between the two factors would be very slight, because the ether extract is a small number. With oats and Indian corn, however, the difference would amount to several calories. In the case of oils in general, the calories of combustion vary greatly with the character of the glycerids. It has been shown, for instance, that a gram of oleomargarin when burned in oxygen affords about 200 more calories than a gram of butter-fat. The natural oils which exist in plants vary in respect of their calorific values. Linseed oil, for instance, has a slightly higher calorific value than olive oil. In Volume III of "Principles and Practice of Agricultural Analysis," p. 569, it is recommended to use the factor 9300 as an approximately correct expression of the heat value of a gram of glycerids. This is probably not far from the correct number for the average of animal and vegetable glycerids, being possibly a little too low. Since in natural cereals we have to do only with vegetable glycerids, and in breads often with a mixture of vegetable and animal glycerids, it is difficult to determine in every case the magnitude of the factor to be employed. For the pure cereal glycerids, however, it is recommended that the factor mentioned above be used; *viz.*, 9300 calories per gram. In the baking of bread, the fats, especially those in the crust, are subjected to a high temperature, under which they possibly undergo a preliminary oxidation. In this case, therefore, the factor given in the "Principles and Practice of Agricultural Analysis," *viz.*, 9300 calories per gram, may be too high.

In the ether extract of cereals there are other bodies besides fat, and it would not be proper to regard the whole mass as having the same fuel value as pure fat. It is difficult to make any accurate allowance for these bodies, which are, moreover, of an organic nature, and capable of yielding considerable quantities

of heat on combustion. To avoid confusion it may be said that the factor 9300 calories per gram may be used also with the ether extracts of flours and meals as well as with those of the baked products. In the sample of ground wheat already mentioned the ether extract is 2.00 per cent. The calories afforded by the oil in burning one gram of flour are therefore

$$0.020 \text{ gram} \times 9300 = 186 \text{ calories.}$$

It is evident that it is impracticable to make any account in our calculations of the heat of combustion arising from the oxidation of the small quantities of coloring-matters, organic acids, and other bodies not included in the above data. By using the factor 9300 for the multiplication of the ether extract instead of the factors determined by direct investigation it is evident that a sufficient allowance will be made for the inclusion not only of the bodies mentioned, but also of the lecithins remaining unextracted, and for which the calorific value approximates that of the true glycerids. The above data then give the basis for calculating the entire calorific power of a whole wheat flour having the following composition :

	Per cent.
Carbohydrates { Starch, cellulose, etc., 68.5 Pentoses 4.5 Sucrose 1.0 } .....	74.00
Proteids.....	10.71
Amids.....	0.48
Oil.....	2.00
Ash .....	2.00
Moisture .....	10.81
	calories.
Calories due to starch, cellulose, etc.....	2877
“ “ “ pentosans .....	171
“ “ “ sucrose. ....	40
“ “ “ proteids .....	632
“ “ “ amids .....	16
“ “ “ oil .....	186
Total calories in one gram .....	3922

#### COMPARISON OF CALCULATED AND ASCERTAINED CALORIES.

The principles of calculation which have been developed above have been applied in the direct comparison of the calories of combustion ascertained by experiment and those calculated

from analytical data. The samples of cereals examined consisted of two samples of wheat, one of rye, one of unhulled oats, and one of hulled barley. The analytical data obtained by careful analyses follow :

CHEMICAL COMPOSITION OF SAMPLES OF GRAIN.

	Wheat No. 1. Per cent.	Wheat No. 2. Per cent.	Rye. Per cent.	Unhulled Oats. Per cent.	Hulled Barley. Per cent.
Moisture .....	11.33	10.65	11.71	9.26	12.20
Ash .....	1.69	1.77	2.31	3.78	0.93
Ether extract.....	2.00	2.24	1.63	4.72	0.92
Protein.....	12.19	14.44	11.69	9.63	10.44
Sucrose.....	0.33	0.48	0.42	0.17	0.18
Invert sugar .....	0.027	0.08	0.068	0.031	0.017
Galactin and dextrin	0.160	0.25	0.220	0.260	0.140
Pentosan .....	5.80	5.17	8.10	13.65	6.50
Fiber .....	2.15	2.56	2.36	12.81	0.80
Starch .....	64.51	62.69	61.78	45.98	68.03

The calculated calories for each of the samples given above are as follows :

CALORIES IN SAMPLES OF GRAIN.

Component parts.	Wheat No. 1. Per cent.	Wheat No. 2. Per cent.	Rye. Per cent.	Unhulled Oats. Per cent.	Hulled Barley. Per cent.
Ether extract .....	186	208	152	439	86
Proteids .....	719	852	690	568	616
Pentosans.....	220	196	308	519	247
Sucrose .....	13	19	17	7	7
Starch and fiber .....	2800	2741	2694	2469	2891
	—	—	—	—	—
Totals .....	3938	4016	3861	4002	3847

The calories found by direct combustion in oxygen were as follows :

Wheat No. 1.. .....	3,922
Wheat No. 2.....	4,011
Rye .....	3,909
Oats.....	4,181
Barley .....	3,886

The direct comparison of the two numbers is seen in the following table :

## COMPARISON.

Variety of grain.	Calculated. calories.	Found. calories.	Difference. calories.
Wheat No. 1.....	3,938	3,922	+16
Wheat No. 2.....	4,016	4,011	+ 5
Rye .....	3,860	3,909	-49
Oats.....	4,002	4,181	-179
Barley .....	3,846	3,886	-40

In the above data all the nitrogen has been computed as protein.

The agreement between the calculated calories and those actually determined in the bomb is satisfactory in the above cases with the exception of the sample of oats. In this case, as will be seen, the calories directly ascertained were 179 greater than those calculated from the analytical data. This fact suggests the possibility of the heat of combustion of the unseparated complex representing the unidentified carbohydrates of hulls and fodders being higher than for starch. Where such a difference exists the suggestion at once occurs that either the analytical data or the calories obtained by combustion are in error. One of the principal values of ascertaining the calories of combustion in analytical work is indicated by such a difference. The combustion will be a check on the analysis, and vice versa the analysis a check on the combustion. Where the differences are as great as noted, the indications are for a repetition of both the analysis and the combustion. The magnitude of the difference between the calculated and ascertained calories which can be allowed as fully within the ordinary errors of analysis and combustion can only be fixed by a long series of determinations, and perhaps after the factors employed for the calculations have been slightly changed to harmonize more closely with ascertained results. At the present time, we are inclined to the opinion that when the difference between the calculated calories and those ascertained on combustion does not exceed fifty to seventy-five calories, the check is sufficiently satisfactory.

We have applied the above process to the investigation of some of the cereal products; *viz.*, flour, bread, breakfast and partially prepared foods and some miscellaneous products. The data which are given below include all of the determinations made on the products mentioned with the exception of six,

where the difference between the ascertained and calculated calories was so great as to indicate an error in one or the other.

The following table contains all the data showing a comparison between the calculated and ascertained calorific power of the several substances mentioned :

COMPARISON OF CEREAL PRODUCTS.

Name of substance.	Determined calories per gram.	Calculated calories per gram.	
		N×5.70.	N×6.25.
Flapjack flour .....	3700	3776	3790
Pancake flour .....	3820	3833	3845
Griddle-cake flour .....	3724	3706	2719
Patent flour.....	3870	3880	3894
Mean .....	3779	3779	3812

BREAD.

Vienna .....	4420	4372	4394
Vienna.....	4381	4339	4359
Home-made.....	4558	4483	4503
Home-made.....	4436	4450	4465
Mean .....	4449	4411	4430

BREAKFAST AND PARTIALLY PREPARED FOODS.—WHEAT PRODUCTS.

Shredded whole wheat biscuit	4253	4298	4314
Wheat germ meal.....	4362	4404	4420
Gluten butter wafers.....	4610	4605	4628
Whole wheat gluten.....	4544	4542	4566
Cooked gluten.....	4432	4406	4425
Germea.....	4445	4403	4417
Breakfast gem .....	4379	4405	4420
Cracked wheat.....	4453	4395	4413
Mean .....	4435	4432	4450

MISCELLANEOUS.

Kaffee-brod .....	4146	4203
Granula .....	4385	4399
Imperial granum.....	4485	4462
F. F. V. malt food .....	4470	4465
Granulated barley .....	4365	4353
H-O oatmeal.....	4800	4799
Mean .....	4442	4447

A study of the above data reveals the fact that while the variations in individual instances are considerable, a comparison



of the means shows that the factors which have been adopted must be very nearly correct, inasmuch as the mean calculated calories differ very little from those determined by actual combustion. In calculating the calories for wheat products both the factors 5.70 and 6.25, for converting nitrogen into proteid matter, have been used. Inasmuch as the calorific power of the protein is slightly greater than that of the carbohydrates, the total calories as calculated by the factor 6.25 are slightly greater than those calculated by the factor 5.70. In the case of breads and other baked products the differences are not so great as we had anticipated, on account of the difficulty of completely extracting the fat and oil from a bread. The individual differences, as in the case of a flour, are somewhat marked, but the means agree very closely.

While this paper was writing, in point of fact on August 2, we received Bulletin 35 of the Wyoming Station (June 1897) in which Prof. Slosson has called attention to work similar to ours which he has done at that station. The factors used by Prof. Slosson differ slightly from those which we have adopted, his factor for fat and oil being 9500, for protein 5700, and for carbohydrates 4200. In nineteen samples of wheat products the calculated calories from analytical data by our factors are 4472, and by Slosson's factors 4447. In six samples of miscellaneous cereal products, calculated by our factors, the number is 4833, and by his, 4810.

It is seen by the above that the mean results are not very greatly different from the two sets of factors, Slosson gaining in his higher factor for fat a portion of what he loses in his lower factor for protein as compared with our numbers.

In conclusion we beg to call attention to the fact that in the light of the data which have been presented in the above paper, we can with reason claim that the determination of the calorific power by combustion under pressure in oxygen is destined to be a valuable aid to the analyst in serving as a check upon the analytical data. We are further warranted in believing that whenever the calculated calories and the analytical data in hulled cereals and cereal products differ by as much as 100 from those obtained by combustion, the chemist will do well to repeat both the analysis and the combustion in order to discover the source

of error. The bomb calorimeter in this way becomes a valuable adjunct to the chemist in his work from a purely analytical point of view.

The data of heat determinations in bodies rich in cellulo-ligno-lignin matters such as bran, hay, straw, and fibers generally, are found to be regularly higher than when calculated from the data of analysis, and this leads us to the belief that these bodies exist in a state of greater molecular condensation than starch. If this be the case, the determination of the heat of combustion may prove helpful in approximately fixing the molecular weight of the polymers in any series insoluble in reagents without change. This subject we are now investigating, and it will form the theme of a subsequent communication.

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## PRELIMINARY NOTE ON SOME NEW DERIVATIVES OF VANILLIN.

BY A. E. MENKE AND W. B. BENTLEY.

Received March 5, 1908.

WHEN chlorine is allowed to act for some time on a solution of vanillin in chloroform, a white crystalline substance is formed, which after suitable purification and analysis was found to be chlorvanillin, melting-point  $166^{\circ}$ .

If chlorvanillin in small quantities be treated with sodium amalgam, chlorvanilloin can be obtained, melting-point  $255^{\circ}$ . We have not yet succeeded in obtaining chlorvanillin alcohol. Fusion of chlorvanillin with caustic potash seems to yield chlorprotoocatechuic acid, melting-point about  $235^{\circ}$ .

The action of dilute nitric acid in suitable proportion upon vanillin yields three products: a white substance containing nitrogen, almost insoluble in the usual solvents, melting-point about  $300^{\circ}$ ; a yellow compound soluble in hot alcohol, almost insoluble in water, melting-point  $178^{\circ}$ – $179^{\circ}$ ; and dinitroguaiacol, melting-point  $123^{\circ}$ , soluble in water. The substance melting at  $178^{\circ}$  is either nitrovanillin or an addition compound of nitrovanillin and dinitroguaiacol. By treatment with nitric acid it yields dinitroguaiacol, and by oxidation with permanganate forms nitrovanillic acid, melting-point  $214^{\circ}$ .

In an attempt to prepare chlorprotoocatechuic acid, directly from protococatechuic acid, we found that passing chlorine in excess

through an alcoholic solution of protocatechuic acid we obtained a resinous matter, which yielded, upon treatment with caustic potash, a substance that could be precipitated by water. This body crystallizes well from alcohol in white crystals, melting-point about  $178^{\circ}$ . Analysis showed it to be tetrachlorpyrocatechin. By varying the strength of the solution of protocatechuic acid, we obtained a different product. The fuller study of these compounds is in progress, and the complete results will be published in a later paper.

ARKANSAS INDUSTRIAL UNIVERSITY.

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### NEW BOOKS.

INTRODUCTION TO ELECTROCHEMICAL EXPERIMENTS. BY DR. FELIX OETTEL, translated (with the author's sanction) by EDGAR F. SMITH. Philadelphia: P. Blakiston, Son & Co. 1897. 144 pp. Price 75 cents.

THE FREEZING-POINT, BOILING-POINT, AND CONDUCTIVITY METHODS. BY HARRY C. JONES. Easton, Pa.: The Chemical Publishing Co. 1897. vii + 64 pp. Price 75 cents.

The great development of physical chemistry in the last few years is calling into existence a considerable literature upon the subject, and it is a happy fact that much of this literature is of the nature of monographs. In this way each author writes from his own experience rather than by compilation, and his writing is correspondingly valuable. Such is the character of the two brief works before us.

Dr. Oettel's book is best described by the opening sentence of the translator's preface: "The purpose of this little volume is to furnish technical chemists and all persons interested in the applications of electricity in chemical manufacture with a concise guide, containing in a compact form all that is essential for the comprehension and solution of problems arising in this comparatively new field of chemical investigation." Its usefulness is wider however, for it lays down principles which are at the basis of electrochemistry not only in technology, but also in analysis and in research work in pure chemistry. The first sixty pages are devoted to the source, measurement, and regulation of the current; then follow the arrangement of experiments, with reference to vessels, diaphragms, electrodes, etc.; phenomena observed in electrolysis, including decomposition pressure, cur-

rent efficiency, transference of ions, etc.; preliminary experiments; calculation of necessary power; and lastly about forty pages of "practical part" including as a practical problem the working of an arsenical copper liquor. The book will be useful in every laboratory where any electrochemical work is done. It is almost needless to add that a translation by Dr. Smith is well done.

Dr. Jones' book, as indicated by its title, is confined to those three physical-chemical methods which find most frequent application in the laboratory. The descriptions of the freezing-point and the boiling-point methods are each preceded by a brief historical sketch and a theoretical discussion of the method, including the processes of calculation. Under the application of the freezing-point method to the determination of molecular weights, the apparatus of Beckmann and its manipulation is carefully described, and in its application to the measurement of electrolytic dissociation, the method of work with the author's apparatus is given. Similarly under the boiling-point method the apparatus of Beckmann, Hite, and that of the author are described, and a detailed account of the method of carrying out a determination follows. Under the conductivity method, the theory is also first discussed and then its application to the measurement of electrolytic dissociation. This book thus brings together in brief space the essentials of theory and practice of these three methods, and is a valuable guide to students in laboratories of physical chemistry.

Both books are of excellent typography, have very complete tables of contents, and neither has an index.

JAS. LEWIS HOWE.

PRACTICAL EXERCISES IN ELECTROCHEMISTRY. BY DR. FELIX OETTEL. Translated by EDGAR F. SMITH, Professor of Chemistry in the University of Pennsylvania. Twenty illustrations. Philadelphia: P. Blakiston, Son & Co. 1897. vii + 92 pp. Cloth. Price 75 cents.

Electrochemistry is becoming year by year of more importance and assistance to the analyst and manufacturer, and any work, historical or descriptive, that adds to our knowledge of the subject is to be commended. The book in question is no more than its name indicates, but it is all that it indicates, for the exercises and examples given are not only practical and simple, but are

most clearly and lucidly set forth. As the translator says in his preface, "The examples given are not only simple, but they are also types of definite processes." Starting with suggestions as to current sources and general apparatus, there follow chapters on the testing and calibration of measuring apparatus, the influence of current density, concentration, temperature, etc., upon the fall of bath-pressure in the electrolyte, influence of current density and concentration on the course of reactions, application of gas analysis to electrochemical reactions, experiments with a diaphragm, metal precipitations with soluble and insoluble anodes, experiments with molten electrolytes, and with multipolar electrodes. The last chapter on organic electrolysis is by Prof. Dr. K. Elbs. The book should be used by all teachers and students in this field and Dr. Smith is to be thanked for giving us this excellent translation.

W. WALLEY DAVIS, JR.

LABORATORY EXPERIMENTS ON THE CLASS REACTIONS AND IDENTIFICATION OF ORGANIC SUBSTANCES. BY ARTHUR A. NOYES, PH.D., and SAMUEL P. MULLIKEN, PH.D. Easton, Pa.: The Chemical Publishing Co. 1897. 8 vo. 28 pp. Price 50 cents.

The authors have collected and thrown into the form of a series of laboratory experiments the various characteristic reactions for different classes of carbon compounds. Workers in organic chemistry gradually acquire a familiarity with these reactions, but the authors have performed a distinct service to the teachers of organic chemistry in bringing them together, where the beginning student can find them, and in emphasizing their importance from an analytical standpoint. This little book might be called the beginning of a qualitative analysis for the carbon compounds, a field which is not yet far advanced.

From this point of view the writer is inclined to regret that the authors did not extend their work beyond the limit of its present twenty-eight pages and make it a more complete collection of the reactions that can be used for the identification of different classes of organic bodies, and supply it with an index so that it would be of use to more advanced workers as well as to the beginners in organic synthesis. The book should find a place in every organic laboratory.

G. M. RICHARDSON.

## **BOOKS RECEIVED.**

**Irrigation Experiments in Sugar Beet Culture.** By Elton Fulmer. Bulletin 31. Washington State Agricultural College, Experiment Station, Pullman, Wash. December, 1897. 30 pp., with a map of Irrigation district.

**The Feeding Value of Salt Marsh Hay.** By J. B. Lindsey and B. K. Jones. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass., January, 1898. 48 pp.

**A Digest of Metabolism Experiments, in which the balance of income and outgo was determined.** By W. O. Atwater and C. F. Langworthy. Bulletin No. 45. Office of Experiment Stations, U. S. Department of Agriculture, Washington, D. C. 1897. 434 pp.

**The Calorific Power of Fuels.** By Herman Poole, F.C.S., New York: John Wiley & Sons. 1898. xv + 255 pp. Price \$3.00.

**Quantitative Chemical Analysis by Electrolysis.** By Dr. Alexander Classen, in cooperation with Dr. Walter Löb. Authorized translation by William Hale Herrick and Bertram B. Boltwood. New York: John Wiley & Sons. 1898. xii + 301 pp. Price \$3.00.

Bulletin No. 10. 1. The Woolly Mullein. 2. The Gape Disease of Poultry. 14 pp. 4 half-tone plates. Bulletin No. 71. 1. Official Analysis of Commercial Fertilizers. 2. Analyses of Other Samples. 10 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 1897.

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[CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, No. 9.]

### THE OXYHALIDES OF ZIRCONIUM.

BY F. P. VENABLE AND CHARLES BASKERVILLE.

Received March 12, 1898.

#### I. ZIRCONIUM OXYCHLORIDES.

WE have examined three of these. The first is secured by the evaporation of an aqueous solution of the salt obtained by dissolving zirconium hydroxide in hydrochloric acid. Very large handsome crystals can be secured on slow evaporation over sulphuric acid. These crystals easily dry on porous plates or on filter-paper. Analysis gave :

Zr.....	28.05
Cl.....	21.59
Loss .....	50.46

This loss represents both water and combined hydroxyl or oxygen. These figures correspond to the formula  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ . One difficulty in the way of securing a correct analysis lies in the constant loss of water on standing exposed to the air. This loss is shown in the following weighings :

	Dates.					
	Oct. 9.	Oct. 11.	Oct. 12.	Oct. 13.	Oct. 15.	Oct. 18.
Weighings.....	1.2806	1.2796	1.2792	1.2787	1.2779	1.2758

By heating to  $135^\circ$ – $140^\circ$  for six hours a large amount of chlorine is driven off and yet not all of the water. The mass is left only partly soluble. Heated to  $100^\circ$  under a stream of hydrogen chloride the weight was constant and the loss corresponded to

26.84 per cent. of the original weight. The residue is entirely soluble in water. Five molecules of water are thus lost at  $100^{\circ}$ , and the compound left is  $\text{ZrOCl}_3 \cdot 3\text{H}_2\text{O}$ . This formula was confirmed by determinations of both  $\text{ZrO}_2$  and  $\text{Cl}$ . The first formula,  $\text{ZrOCl}_3 \cdot 8\text{H}_2\text{O}$ , is the one assigned by Paykull<sup>1</sup> and confirms his results as against those of Melliss.<sup>2</sup> The formula gotten by Herrmann,  $\text{ZrOCl}_3 \cdot 9\text{H}_2\text{O}$ , was manifestly obtained from imperfectly dried crystals.

Various experiments on the dehydration of this salt were carried out. Thus a portion placed in a desiccator over fused calcium chloride had lost a large part of its water and was still losing weight after seven months. Another portion was placed over fused calcium chloride and dry air was drawn over it at the rate of about fifty liters in the twenty-four hours for six months. After the first two months it was examined weekly by the interposition of a flask containing silver nitrate to see whether hydrochloric acid was still coming off. Even after the lapse of so long a time as this it was found that the loss of hydrochloric acid continued although it was very slight. Lastly a portion was placed over concentrated sulphuric acid and the atmosphere above it exhausted occasionally. This was kept up during two months of summer weather. The loss in the last fifteen days was about 0.02 per cent. of the whole. The mass was powdery with a slightly discolored crust. It was all soluble in water, however, and yielded a clear, colorless solution. It contained 53.30 per cent. of zirconium dioxide. This corresponds very nearly to the formula  $\text{ZrOCl}_3 \cdot 3\text{H}_2\text{O}$ .

Another form of the oxychloride is gotten by crystallization from concentrated hydrochloric acid. The form of the crystals is apparently similar to that of the crystals from an aqueous solution. It is difficult to free these from excess of acid. Linemann,<sup>3</sup> by treatment of this with alcohol and ether, secured a fine, crystalline, snow-white, silky body, leaving fifty per cent. of its weight on ignition. This is, however, far from an accurate method for removing the water.

<sup>1</sup> *Ber. d. chem. Ges.*, 6, 1467.

<sup>2</sup> *Ztschr. Chem.* (2), 6, 196.

<sup>3</sup> *Chem. News*, 52, 224.



Bailey<sup>1</sup> tried various methods of drying these crystals without success.

It was found that these crystals could be dried under hydrogen chloride at 100°–125° C. At this temperature a white mass soluble in water was gotten which gave on analysis :

	Calculated for $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$ .	Found.
Zr.....	39.12	38.99
Cl.....	30.66	29.98

The amorphous (?) form, insoluble in concentrated hydrochloric acid, but easily soluble in water, has been analyzed by Paykull, and he has calculated the formula  $2\text{ZrOCl}_2 \cdot 13\text{H}_2\text{O}$ . This insoluble oxychloride is nearly always present during the process of purification by recrystallization from concentrated hydrochloric acid. Repeated boilings with hydrochloric acid fail to dissolve it. A sample was prepared by allowing a very concentrated aqueous solution of the oxychloride to fall drop by drop into concentrated hydrochloric acid. It was washed with hydrochloric acid and then boiled with it. After pouring off the acid the mass was washed with a mixture of nine parts ether and one part alcohol. It was dried between filter-paper. Little assurance could be felt that this mode of drying removed all the hygroscopic moisture. It was analyzed in this condition. Another portion was placed over caustic alkali (after pressing between filter-paper) and yet another portion was dried at 105° in a stream of hydrogen chloride.

The analysis of the portion dried between filter-paper was as follows (no difference was observed in that over caustic alkali after two days) :

	Calculated for $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ .	Found.
Zr.....	31.70	31.72
Cl.....	21.01	20.81

This is therefore in close accord with the formula  $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ . The portion dried under hydrogen chloride was small and only the zirconium was determined. The percentage of this corresponded fairly well with  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$ .

Summarizing our examination of these oxychlorides then, we find that there are three :

<sup>1</sup> *Chem. News*, 60, 17.

1. An oxychloride gotten in large, well-formed crystals by crystallization from water. These crystals lose both water and hydrochloric acid on exposure to the air. Their formula is  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .

2. An oxychloride gotten by precipitation with hydrochloric acid from an aqueous solution. This is insoluble in hydrochloric acid. It is seen in silky crystals or a white mass of very fine crystals. The formula is  $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ .

3. An oxychloride gotten by crystallization from hydrochloric acid. This has the formula  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$ .

When any one of these is dried at  $100^\circ$ – $125^\circ$ , with a stream of dry hydrogen chloride passing over it, three molecules of water of crystallization are left and the oxychloride has the formula given under 3, namely  $\text{ZrOCl}_2 \cdot 3\text{H}_2\text{O}$ . These last molecules of water are lost at a temperature of  $180^\circ$ – $210^\circ$ .

Weibull<sup>1</sup> gives the measurements of the crystals of the oxychloride formed from water. They belong to the tetragonal system, and are optically uniaxial with double refraction.

Several times during the examination of these oxychlorides the formation of a hydrogele was observed. The exact conditions under which it was formed were not determined. The tendency to form this hydrogele is much less than in the case of the bromides and iodides. Similar compounds will be mentioned there.

## II. ZIRCONIUM OXYBROMIDES.

Zirconium oxybromides may be formed by decomposing the tetrabromide with water and also by dissolving zirconium hydroxide in hydrobromic acid.<sup>2</sup> It crystallizes from the aqueous solution in fine, transparent, needle-like crystals containing water of crystallization.<sup>3</sup>

Weibull gives the following analyses :

	Calculated for $\text{ZrOBr}_2 \cdot 8\text{H}_2\text{O}$ .	I.	Found.	II.
Zr .....	21.87	20.35		20.83
Br .....	39.05	41.16		38.70

He says that the crystals are isomorphous with those of the oxy-

<sup>1</sup> *Ber. d. chem. Ges.*, 1887, 1394.

<sup>2</sup> Berthemot : *Ann. chim. phys.*, 44, 393.

<sup>3</sup> Weibull : *Ber. d. chem. Ges.*, 1887, 1394.

chloride which seems to be true. They are much more hygroscopic. His two analyses are decidedly discordant and one would judge that the amount of water of crystallization had been decided upon from the analogy to the oxychloride.

The oxybromides described in the following experiments belong to two types with varying degrees of hydration— $\text{ZrOBr} \cdot x\text{H}_2\text{O}$ , where  $x = 3, 13$  or  $14$  and  $\text{ZrBr(OH)} \cdot y\text{H}_2\text{O}$  where  $y = 1$  or  $2$ . All of these compounds are deliquescent and decompose on exposure to moist air, the clear white crystals, often colored pink by free bromine present, melting to a gum, frequently with the evolution of hydrobromic acid. The salts are unstable even in dry air as was found on exposing dried crystals upon a watch-glass in a desiccator containing sulphuric acid. Much hydrobromic acid was evolved in the decomposition.

The crystals were prepared in two ways: either by dissolving pure  $\text{Zr(OH)}_4$  in dilute hydrobromic acid evaporating upon a water-bath with subsequent additions of forty-eight per cent. hydrobromic acid and repeated evaporation, or a concentrated solution of hydrobromic acid was saturated with  $\text{Zr(OH)}_4$ , evaporated, and the crystals obtained on cooling.

As a rule the crystals obtained were quite soluble in the hot acid but separated at once on cooling. In the heating necessary for the thorough saturation of the hydrobromic acid by the  $\text{Zr(OH)}_4$ , the solution first becomes straw-colored then a deeper red, depending upon the time of the heating. This is evidently due to bromine from the decomposition of some hydrobromic acid.

A difficult problem was the removal of the strong hydrobromic acid mother-liquor and the free bromine nearly always present with the crystals. Of the methods tried to effect this, none proved satisfactory. The crystalline mass in one case was six times washed with ether, the yellowish-red solution, due to dissolved bromine, being decanted. Filtering proved too slow, permitting a rather long exposure of the crystals to the moisture of the air. After this washing with ether the crystals, still slightly yellow colored, were placed in a vacuum desiccator for the removal of the remaining ether. The small glass dish containing the material was allowed to remain thirty-six hours

in the vacuum desiccator. The substance was then removed, dried between filter-paper, and analyzed.

	Calculated for $\text{ZrOBr}_2 \cdot 13\text{H}_2\text{O}$ .	I.	Found. II.	III.
$\text{ZrO}_2$ .....	24.01	24.15	24.50	24.60
Br .....	31.93	....	32.29	....
Loss at $124^\circ \text{C}$ . less HBr evolved..	....	....	24.44	....

This substance gave evidence of decomposition after being placed in the weighing bottle.

Another method used for the removal of bromine was washing the colored crystals three times with strong (forty-eight per cent.) solution of hydrobromic acid. Most of the bromine was thus removed although the salt remained slightly yellow, possibly due to the remaining hydrobromic acid. An interruption of the work at this point required the salt in this state to be placed in a desiccator over sulphuric acid. It remained there for several days when the work was resumed. All moisture seemed to be removed and great volumes of hydrobromic acid were given off when the desiccator was opened. The substance had taken on a brownish-red color around the edges but the central portion was perfectly white. To remove the excess of acid the substance was washed quickly three times with small amounts of water. All of these salts are exceedingly soluble in water and the utmost care is necessary to avoid the entire re-solution of the substance. The wash-water was deeply colored by the bromine removed and the salt remained pinkish. It was dried on filter-paper and an analysis gave 24.54 per cent. zirconium dioxide.

This shows that the method of removing the bromine and hydrobromic acid and drying the crystals, did not materially alter their composition. Alcohol did not give satisfactory results.

The ether-washed crystals, after being allowed to stand in a glass-stoppered weighing bottle in the balance case for several weeks, showed evidence of absorbed moisture. They were dried again by pressure between folds of bibulous paper, but they could not in this way be brought back to the same state as before, as shown by the analysis :

	Calculated for $\text{ZrOBr}_2 \cdot 14\text{H}_2\text{O}$ .	Found.	Previously found.
$\text{ZrO}_2$ .....	23.70	23.49	24.50(av.)
Br .....	30.82	30.58	.....

About four grams of these crystals were dried in a glass-stoppered flask under a rapid stream of dry hydrobromic acid at a temperature varying between  $100^{\circ}$  and  $120^{\circ}$ . The average temperature was about  $110^{\circ}$ , and the drying lasted continuously through three and a half days. After cooling, perfectly dry air was drawn through the flask for a little over ten minutes. This was supposed to be [but was not long enough as the analysis showed that all the free hydrobromic acid had not been removed. It requires at least thirty minutes for thorough removal. The substance dried down to a hard, white, crystalline solid which was quite soluble in water. The composition of this salt was as follows :

	Calculated for $\text{ZrOBr}_2 \cdot 4\text{H}_2\text{O}$ .	I.	Found. II.
$\text{ZrO}_2$ .....	36.21	34.91	34.82
Br .....	47.30	50.05	....

It is evident that the assignment of such a formula is largely guess work, but the cost in time and materials was too great for us to repeat the experiment.

Another experiment was carried out as follows :

One hundred cc. of forty-eight per cent. hydrobromic acid solution were saturated with wet  $\text{Zr}(\text{OH})_4$  by continuous boiling. The solution was never perfectly clear until it was twice filtered through compact filter-paper doubly folded. The clear yellow solution was concentrated by evaporation on the water-bath. The more concentrated it became the redder it was; finally the color was so deep that it appeared almost black. This was due to decomposition of the hydrobromic acid.

After concentration the liquid was cooled and white crystals separated out. On allowing it to stand twenty-four hours, or always when made too concentrated by further evaporation, a red jelly separated on top of these crystals. In trying to wash this jelly from around the crystals, for it was very soluble in water, the crystals were also dissolved. The whole was therefore redissolved and after several attempts a set of prismatic needles one to two mm. in length separated free from the jelly. This jelly was not silicic acid as feared. The mother-liquor was poured off, the crystals quickly washed three times with small amounts of water, dried between filter-paper, and analyzed:

	Calculated for $\text{ZrBr}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ .	I.	Found.	II.
$\text{ZrO}_2$ .....	35.23	34.90		34.34
Br .....	31.01	30.79		....

The solution was further evaporated and another crop of needle crystals similar to, but much smaller than, the above obtained. They were washed four times in cold water, dried to a powder between filter-paper and analyzed :

	Calculated for $\text{ZrBr}(\text{OH})_3 \cdot \text{H}_2\text{O}$ .	I.	Found.	II.
$\text{ZrO}_2$ .....	37.91	36.86		36.35
Br .....	33.33	32.49		....

An investigation of the gelatinous oxybromide of zirconium showed that it was a hydrogele. On dialysis the small amount of crystalline oxybromide present passed through the membrane. At the same time the gelatinous compound, if it may be so termed, slowly decomposed into zirconium hydroxide and hydrobromic acid, the latter gradually passing through the septum while the former remained behind.

### III. ZIRCONIUM OXYIODIDES.

According to Melliss, zirconium oxyiodide is not formed by dissolving  $\text{Zr}(\text{OH})_4$  in hydriodic acid. Hinzberg<sup>1</sup> secured an oxyiodide by precipitating a solution of zirconium sulphate with barium iodide in equivalent amounts. The solution was evaporated over sulphuric acid and the crystals washed with carbon bisulphide. The analysis gave  $\text{ZrI}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ .

In our experiments we found that zirconium hydroxide, when precipitated cold, was soluble to a small extent in strong aqueous hydriodic acid or could be dissolved by passing hydrogen iodide into water in which the zirconium hydroxide was suspended. Evaporation of this solution over sulphuric acid or calcium chloride gave needle-like crystals strongly colored with iodine and very hygroscopic. Every attempt failed at getting these freed from excess of iodine and properly dried. Washing with ether or with carbon bisulphide was ineffective. A hydrogele was gotten by acting upon zirconium hydroxide with hydrogen iodide, which formed on drying a hard, horn-like, colored mass insoluble in water and acids. This contained :

<sup>1</sup> *Ann. Chem.* (Liebig), 239, 253.

	Per cent.
Zr.....	32.14
I.....	27.88
H <sub>2</sub> O (by difference) .....	28.64

It lost only 11.07 per cent. of its weight after three hours' heating at 100°-120°.

UNIVERSITY OF NORTH CAROLINA.

## ATROPINE PERIODIDES AND IODOMERCURATES.

BY H. M. GORDIN AND A. B. PRESCOTT.<sup>1</sup>

Received March 12, 1898.

### I. ATROPINE ENNEAIODIDE.

It has been known for a long time that in solutions of atropine salts, as in those of the salts of most other alkaloids, a solution of iodine in potassium iodide gives an insoluble precipitate. The nature of this precipitate has so far as we know not been thoroughly investigated. Jörgensen<sup>2</sup> has obtained and described two periodides of atropine: a triiodide and a pentaiodide. Our experience has taught us that in aqueous solutions the capacity of atropine for combining with iodine varies very widely, and the quantities taken up seem to depend upon the concentration of the liquids and even the order of mixing them.

The highest number of iodine atoms which a molecule of atropine can combine with, seems to be nine; between this and the above-mentioned triiodide lie the other compounds of atropine with iodine which are formed in aqueous solution. The same is true when chloroform is used as a solvent. We reserve for a later date a report upon the exact conditions which are necessary for the formation of any particular periodide of atropine. For the present we wish to say that under the conditions described below we were able to obtain the enneaiodide of atropine, C<sub>17</sub>H<sub>21</sub>NO<sub>9</sub>.HI.I<sub>9</sub>, as the sole combination of all the alkaloid, and sufficiently stable.

These conditions are the following: The concentration of the aqueous solution of the atropine salt should not exceed five-tenths per cent.; that of the iodine solution must not exceed one

<sup>1</sup> In the work of Research Committee D, Section 2, Committee on Revision of the Pharmacopeia of the United States.

<sup>2</sup> *J. prakt. Chem.* [2], 3, 329.

per cent. ; the latter has to be acidulated with some sulphuric or hydrochloric acid ; the atropine solution must be added to the iodine solution and not *vice versa*, and this addition must take place in small portions at a time, shaking the mixture thoroughly after each addition. At first the liquid becomes very turbid and particles of iodine are seen to be floating upon its surface ; on continued addition of the atropine solution and shaking, the iodine-colored turbidity disappears, a dark granular precipitate falls out, and the supernatant liquid becomes perfectly transparent but is still dark-colored. If the addition of the atropine be stopped at this stage, *i. e.*, while the supernatant liquid has a very dark red color, the composition of the precipitate will be found to be that of the enneaiodide  $C_{17}H_{11}NO_5HI.I_9$ .

Whether additional quantities of atropine will make the precipitate take up more atropine and become a lower periodide we shall try to determine by later experiments. On the other hand when the order is reversed and the iodine solution is added to the atropine solution, it is always a lower periodide that is formed ; but whether on continued addition of the iodine the precipitate will take up more of it and become a higher periodide, we cannot say as yet.

The enneaiodide, obtained as described, being unstable while moist and when removed from its mother-liquor, the precipitate has to be collected quickly by means of a pump, washed a few times with cold water and dried first on porous plates and then in vacuum over sulphuric acid. As thus obtained it is a very dark brown almost black powder, quite permanent in dry air and has only a slight odor of iodine. It is very difficultly soluble in ether, chloroform, benzene, or carbon disulphide, but is soluble in alcohol, very freely when hot. In cold water it is insoluble ; hot water decomposes it quickly ; it is also decomposed by concentrated solutions of potassium iodide. At  $90^{\circ}$  C. it commences to give up iodine vapors and at  $140^{\circ}$  C. melts to a dark liquid.

To obtain it in crystalline form it is first washed with a little cold alcohol to remove traces of free iodine and then dissolved in warm alcohol. On cooling it crystallizes out in dark-green prisms and leaflets, having the same properties as the non-crystallized body.



In this enneaiodide one-ninth of the total iodine is firmly combined just as in normal hydriodides, while eight-ninths is easily removed by reducing agents, such as sulphur dioxide and sodium thiosulphate. The compound therefore may be considered an atropine hydriodide octaiodide.

The additive iodine we estimated volumetrically and the total iodine both gravimetrically and volumetrically.

To estimate the additive iodine a small quantity of the enneaiodide is dissolved in very little alcohol, an excess of a standardized solution of sodium thiosulphate added and the excess titrated back with a standard solution of iodine using starch as the indicator.

For total iodine the substance is covered with an excess of powdered metallic zinc and some water and then boiled gently for ten or fifteen minutes, taking care to prevent loss by spurting; the mixture is then thrown upon a filter, and the containing flask and the filter thoroughly washed with hot water. The iodine in the zinc iodide thus formed can either be estimated by precipitation with silver nitrate and nitric acid and weighing as silver iodide, or it is precipitated with an excess of a standardized solution of silver nitrate and the excess titrated back with a standard solution of ammonium thiocyanate, using ferric nitrate as indicator.

Having obtained the enneaiodide of atropine it was natural to suppose the existence of a heptaiodide, with probability of a complete series from the triiodide to the enneaiodide. And in fact in the course of our work we once obtained this heptaiodide. But our efforts to determine the exact conditions necessary for the formation of this body have so far not been successful.

The easiest way to obtain the periodides of atropine is to use chloroform as a solvent. On adding twenty grams atropine to a warm solution of thirty grams iodine in chloroform (500 cc.) the enneaiodide crystallizes out very soon in the shape of small, shining, dark green crystals. If these be removed by filtration, the mother-liquor will give several successive crops of the dark blue pentaiodide and at last a crop of the brownish-red triiodide.

## II. ATROPINE MERCURIC IODIDES.

The periodides of atropine, like those of many other alkaloids,

easily give double salts with mercuric iodide, obtained on shaking the alcoholic solution of the periodide with mercury and gently warming the mixture. This double iodide of atropine and mercury can also be made by mixing theoretical quantities of atropine and iodine, adding a little alcohol and an excess of mercury, slightly warming, and shaking till the color of iodine disappears. If the higher periodides of atropine be used in the preparation of this double iodide of atropine and mercury there is always separation of mercurous iodide; but if theoretical quantities of atropine and iodide are used there is no separation of mercurous iodide. The formula of this double iodide of mercury and atropine, as shown by our analysis, seems to be  $C_{17}H_{23}NO_3.HI.HgI_2$ . It resembles in composition several other double iodides of alkaloids and mercury obtained by Groves<sup>1</sup> by a different method. But besides this double iodide we also obtained another having the composition  $(Atrop.HI)_2.HgI_2$ . It was made by treating a solution of the  $Atrop.HI.HgI_2$  in diluted alcohol with an excess of potassium iodide. From the liquid obtained by shaking an alcoholic solution of atropine and iodine with mercury the monoatropine hydriodide mercuric iodide crystallizes out in shining yellow crystals, melting at  $89^\circ$  to  $90^\circ$  C., difficultly soluble in ether or chloroform, partly soluble in hot water, and very soluble in warm alcohol. The diatropine hydriodide mercuric iodide obtained as said above by the action of potassium iodide on the mono compound, crystallizes in perfectly white, silky needles, which on being dried assume a yellowish tint. They melt at  $98^\circ$  to  $99^\circ$  C., are very easily soluble in warm alcohol, and quite soluble in hot water.

The analysis for mercury and for iodine in these bodies can be made in different ways, but the best results are obtained by a modification of the method of Risse.<sup>2</sup> The mercury and the iodine are determined in two separate portions. For mercury the substance is dissolved in a little warm alcohol and a little water added; the solution is then acidulated with a few drops of dilute hydrochloric acid and saturated with hydrogen sulphide. The mercuric sulphide is then dried and weighed in the usual way. For the determination of iodine the substance is treated

<sup>1</sup> *Quart. J. of Chem. Soc.*, 11, 97.

<sup>2</sup> *Ann. Chem. (Liebig)*, 107, 223.

with a hot solution of potassium hydroxide (1 : 10), diluted with water, filtered, and when completely cold neutralized with acetic acid. The iodine is now precipitated with silver nitrate and nitric acid and determined as silver iodide in the usual way.

In the following analyses the standard silver nitrate solution was made to correspond with one per cent. of iodine and the ammonium thiocyanate solution to correspond, cc. per cc., with the silver nitrate solution. The standard solution of iodine contained one per cent. of iodine and the sodium thiosulphate solution corresponded, cc. per cc., with the iodine solution.

*Analysis of the Atropine Enneaiodide not Recrystallized*: Volumetric estimation for total iodine, 0.15225 gram required 12.2 cc. of the silver nitrate solution.

For the iodine removed by reduction, 0.19255 gram required 13.7 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_9 \cdot HI \cdot I_8$ .	Found.
Iodine by reduction .....	70.88	71.15
Total iodine .....	79.74	80.13

In the gravimetric estimation from 0.218 was obtained 0.3207 silver iodide.

	Calculated for $C_{17}H_{23}NO_9 \cdot HI \cdot I_8$ .	Found.
Total iodine .....	79.74	79.48

*Analysis of the Atropine Enneaiodide Recrystallized from Alcohol*: The methods employed were the same as with the non-recrystallized compound and the standard solutions of the same strength.

In the volumetric estimation of total iodine, 0.12685 gram required 10.1 cc. of the silver nitrate solution. For the iodine removed by reducing agents, 0.23105 gram required 16.4 cc. of the thiosulphate solution.

	Calculated for $C_{17}H_{23}NO_9 \cdot HI \cdot I_8$ .	Found.
Total iodine .....	79.74	79.62
Iodine by reduction .....	70.88	70.98

In the gravimetric estimation of total iodine, 0.2031 gram gave 0.30035 silver iodide.

	Calculated for $C_{17}H_{23}NO_9 \cdot HI \cdot I_8$ .	Found.
Total iodine .....	79.74	79.90

*Analyses of the Double Salts of Atropine Hydriodide and Mercuric Iodide:* 0.2632 gram of the monoatropine hydriodide mercuric iodide gave 0.0699 gram mercuric sulphide, and 0.30445 gram of the substance gave 0.24785 gram silver iodide.

	Calculated for Atrop. HI.HgI <sub>2</sub> .	Found.
Mercury.....	23.03	22.89
Iodine .....	43.74	43.98

Of the diatropinehydriodide mercuric iodide, 0.1798 gram gave 0.032 gram mercuric sulphide, and 0.257 gram of the substance gave 0.18885 gram silver iodide.

	Calculated for (Atrop.HI) <sub>2</sub> .HgI <sub>2</sub> .	Found.
Mercury .....	15.58	15.34
Iodine .....	39.46	39.70

### III. ATROPINE ESTIMATION AS PERIODIDE.

The formation of atropine enneaiodide under the conditions described above affords a convenient method for estimating the strength of atropine solutions by means of a standard solution of iodine and titrating back with a standard solution of sodium thiosulphate. The way to operate is as follows: The atropine solution, whose strength is approximately determined by a preliminary experiment, operating in the way described below, is diluted with water so as to contain at most four-tenths to five-tenths per cent. of the alkaloid and in so doing the solution is made up to a given volume. Twenty or thirty cc. of a decinormal iodine solution are now put into a measuring flask holding 100 cc., diluted with a little water, and acidulated with a few drops of diluted sulphuric acid; the atropine solution is now run in from a burette slowly, and in small portions at a time, shaking the flask thoroughly after each addition and observing whether the supernatant liquid commences to clear up. If not, a little more of the atropine solution is added, and the mixtures again shaken for a minute or two. In this way the addition of atropine is slowly continued till after a few shakings the supernatant liquid commences to become transparent, still having a dark red color, which can easily be seen by stoppering the flask, reversing it and looking through its neck. The addition of atropine is then stopped, the flask shaken till the supernatant liquid

is perfectly transparent, and then it is diluted to 100 cc. Of this liquid an aliquot portion is filtered off and the excess of iodine in it determined by a decinormal solution of sodium thiosulphate. Every part by weight of iodine consumed corresponds to 0.2849 part of alkaloid or every cubic centimeter of the decinormal iodine solution consumed corresponds to 0.0036048 gram of atropine alkaloid.

These factors are obtained on the ground that for the formation of the atropine enneaiodide only eight atoms of iodine are supplied by the free iodine used to make the decinormal iodine solution, the ninth atom coming from the potassium iodide of that solution. The success of this method depends solely upon the atropine solution being sufficiently diluted, as otherwise a resinous mass is liable to be formed instead of a granular precipitate, and added in small portions at a time to the iodine solution, care being taken to shake the mixture after each addition and to stop the operation as soon as the supernatant liquid commences to become transparent, being still red-colored. It is easy to be guided by the very dark color, as an excess of atropine makes the liquid almost colorless. With a little care the method gives very good results, as can be seen from the following analyses.

Whether this method of assay is applicable to the crude drugs containing atropine and their galenical preparations, we shall try to determine by experiments to be continued.

In conclusion we wish to say that the method of using a solution of iodine and potassium iodide for the quantitative estimation of alkaloids has been long since proposed,<sup>1</sup> and recently Kippenberger<sup>2</sup> has given considerable prominence to this method in his toxicological and other researches. But he rests upon the assumption of the formation of the atropine triiodide, and this may be the leading product under the particular conditions he prescribes; but his method as a whole, when tried in this laboratory, has not given satisfactory results. The estimation of caffeine as a periodide recently published by Gomberg<sup>3</sup> proves highly satisfactory.

<sup>1</sup> Bouchard: *Compt. rend.*, 9, 475; R. Wagner: *Ding. poly. J.*, 161, 40; *Ztschr. anal. Chem.*, 1, 102.

<sup>2</sup> *Ztschr. anal. Chem.*, 35, 10; 34, 317, etc.

<sup>3</sup> This Journal, 18, 337.

In the following estimation of the strength of atropine solutions both the iodine solution and the sodium thiosulphate solution were strictly decinormal. Of the iodine solution twenty or twenty-five cc. were put into a 100-cc. measuring flask and atropine solutions of known strength run in from a burette and the operation continued as described above. When the supernatant liquid was perfectly transparent the flask was filled up to 100 cc. and fifty cc. were filtered off. In these fifty cc. the excess of iodine was determined by means of the tenth-normal thiosulphate solution and the strength of the atropine solutions calculated by using the factor 0.0036048 for every cubic centimeter of decinormal iodine used up.

No. of sample.	Number of cc. of the atropine solution taken.	Number of cc. of the tenth-normal iodine used up.	Calculated strength. Per cent.	Actual strength. Per cent.
1	12	15.6	0.47	0.50
2	15	14.9	0.36	0.40
3	17	13.2	0.28	0.30
4	12	10.0	0.28	0.25

We shall try to determine experimentally whether this method is also applicable to other alkaloids and their galenical forms.

The above-mentioned factor for every cubic centimeter of the decinormal iodine solution was deduced as we said upon the ground that only eight atoms of iodine of every molecule of the atropine enneaiodide are furnished by the free iodine of the iodine solution—the ninth atom forming the normal iodine of the enneaiodide coming from the potassium iodide.

That this is really so has been admitted by almost all chemists in the case of all other periodides whose constitution is similar to that of the atropine enneaiodide. It would, therefore, seem to be superfluous to prove experimentally the correctness of this view with regard to the enneaiodide of atropine. But owing to the fact that Kippenberger in the above-cited articles advances a different view we thought it advisable to prove irrefutably that the iodide of potassium of the iodide solution takes an active part in the reaction by which the atropine enneaiodide is formed and gives off an amount of iodine which is just equal to the amount of the normal iodine of the enneaiodide.

We proceeded in the following manner: We first determined the strength of our iodine solution with regard to free iodine;

this was done by means of a sodium thiosulphate solution of known strength. We then took ten cc. of this iodine solution and determined the total amount of iodine, free as well as bound to potassium, by shaking them in a flask with an excess of powdered metallic zinc till the color of iodine disappeared, filtering the solution of zinc iodide and potassium iodide thus obtained, washing the flask and the excess of zinc with hot water and precipitating the iodides in the filtrate with silver nitrate and nitric acid. From the weight of silver iodide, washed and dried in the usual way, we calculated the amount of total iodine present in our iodine solution. By subtracting the amount of free iodine from that of the total iodine we obtained the amount of iodine present in our solution as potassium iodide. We thus found that the iodine solution contained one per cent. free iodine and 1.2312 per cent. combined iodine.

We then put forty cc. of this iodine solution in a 100-cc. measuring flask, added twenty cc. of a three-tenths per cent. solution of atropine alkaloid, and, after shaking well, diluted the liquid in the flask to 100 cc. We now took two vials and in each filtered off twenty-five cc. from the flask. In the first vial the amount of free iodine titrated back with sodium thiosulphate was found to be 0.0465. From this it is easy to deduce that the twenty cc. of the three-tenths per cent. atropine solution consumed 0.214 gram of the free iodine. In the second vial the total iodine was determined in the same way as described above and the quantity of silver iodide was found to be 0.3023 gram which shows that after the treatment with atropine the liquid contained 1.633 per cent. total iodine. From these data we deduce that the twenty cc. of the atropine solution have taken up 0.02528 gram iodine from the bound iodine. As the twenty cc. of atropine solution contained 0.06 gram atropine we find for 100 parts of precipitated enneaiodide

	Found. Per cent.	Calculated. Per cent.
Atropine .....	20.05	20.26
Iodine taken from the free iodine of the iodine solution.....	71.50	70.88
Iodine from the iodine bound as KI..	8.45	8.86

We see that in aqueous acidulous solutions the potassium iodide takes an active part in the reaction by joining in a yield of hy-

hydriodic acid for the normal hydriodide of the alkaloid, necessary to hold the additive iodine of the periodide. When carbon disulphide or carbon tetrachloride is used as solvent for the atropine and the iodine, no periodide seems to be formed, possibly for the reason of there being no generation of hydriodic acid for the making of hydriodide. As to the formation of the periodides in chloroformic solutions of atropine and iodine, it might possibly be explained by the substituting action of iodine either upon the chloroform or upon a side-chain of the atropine.

The direct substitution of iodine for some of the hydrogen in these bodies might, in this case, be made possible by the presence of the natural base which combines with the hydriodic acid, when formed by such a substitution. Part of the atropine would then act in a manner similar to that of mercuric oxide, which is usually employed in the iodizing of hydrocarbons. An analogous case we have in the easy substitution of iodine for some of the hydrogen in aniline, a part of which combines with the hydriodic acid, which is set free through the substitution of iodine for hydrogen in another part. At any rate we shall endeavor to determine the by-products formed when atropine enneaiodide is produced in chloroformic solutions.

UNIVERSITY OF MICHIGAN,  
FEBRUARY 28, 1898.

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## COMPOSITION OF THE ASHES OF SOME RAW TANNING MATERIALS.<sup>1</sup>

BY WM. K. ALSOP AND J. H. YOCUM.

Received March 15, 1898.

NO systematic investigation of tannin sources has been published which covers not only the tannin itself, but also the other chemical compounds found in the raw material. With the object of making a complete analysis of some of the common sources of tannin, we present this paper on the ash and tannin analysis, and hope in the future to present others bearing upon the sugars and other soluble non-tannins, celluloses, and red coloring material.

In the table presented showing the tannin content of oak and hemlock bark, the averages from two widely separated localities for each of a large number of analyses, are given. The method

<sup>1</sup> Read before the New York Section, March 11, 1898.



of determining the tannin followed, was that of the Association of Official Agricultural Chemists for 1897. The total extract is the result obtained by extracting the bark with boiling water and evaporating the solution ; the residue left in the extractor is reported as cellulose and insoluble, and was obtained by difference. A larger total extract can be obtained if alcohol be used as the extracting medium, this increase being of the nature of the red coloring material, hence the residue from a water extraction is not pure cellulose. The total extract (with water) when at 95° C., dissolves a considerable portion of the red coloring material from the bark, they being precipitated upon cooling the solution. The soluble solids are the solids of extract solution soluble at 18° C., and the red coloring material is the difference between total solids and soluble solids. The non-tannins are that portion of the soluble solids not absorbed by hide and are mainly glucosides of unknown composition. Tannins are the difference between soluble solids and non-tannins. Moisture was determined by drying at 100° C. In the table giving the ash analysis, the results, marked Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>, represent practically alumina, as only traces of ferric oxide could be found in the precipitate.

The extract results give the portion of the ash removed by leaching, since it required three portions of bark to make one of extract. During the extraction only 0.44 per cent. of ash was removed from the bark. The very much greater ash of oak over hemlock bark and the higher proportionate amount of lime is no doubt due to the fact that hemlock does not grow on a limestone soil.

	Chestnut-oak bark.	Chestnut-oak bark.	Hemlock bark.	Hemlock bark.	Quebracho wood.	Oak-bark extract.
Number of samples .....	118	117	81	50	1	1
Total extract .....	24.69	19.76	19.33	19.96	24.80	46.92
Total soluble solids.....	20.36	16.26	15.40	16.11	19.20	45.96
Red coloring material.....	4.33	3.50	3.93	3.85	5.60	0.96
Non-tannins .....	9.81	8.21	6.74	6.44	3.64	20.29
Tannins .....	10.55	8.05	8.66	9.67	15.56	25.67
Moisture.....	10.85	9.73	11.57	13.75	11.60	53.17
Cellulose and insoluble matter..	64.46	70.51	69.10	66.29	63.60	....

	Chestnut-oak bark. No. 1.	Chestnut-oak bark. No. 2.	Hemlock bark. No. 3.	Hemlock bark. No. 4.	Quebracho wood. No. 5.	Oak-bark extract. No. 6.	Leached oak bark. No. 1.	Leached oak bark. No. 2.	Leached hem- lock bark. No. 3.
Ash.....	6.02	8.05	1.65	1.45	0.88	1.35	6.35	6.96	1.55
Carbon .....	0.77	0.11	0.23	0.59	0.11	1.57	0.15	0.15	....
Sand and si- licic acid..	2.34	3.33	....	....	0.88	1.88	....	....	7.15
Sand.....	....	....	1.12	3.53	....	....	1.52	1.46	....
SiO <sub>2</sub> .....	....	...	0.78	2.84	....	....	1.40	0.77	....
Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	0.08	0.86	3.07	3.86	0.64	5.59	0.71	0.55	2.05
MnO .....	1.26	0.33	2.26	4.09	0.10	2.21	0.58	0.28	2.41
CaO .....	52.63	58.24	52.52	49.35	61.27	19.15	57.42	60.50	53.97
MgO .....	1.18	1.77	1.98	2.92	4.56	2.38	0.56	1.13	1.68
K <sub>2</sub> O .....	2.95	2.62	6.02	7.64	0.24	29.44	1.77	0.84	2.35
Na <sub>2</sub> O .....	0.63	0.40	0.27	0.95	1.22	1.01	0.44	0.38	0.66
Cl .....	0.44	0.10	0.20	0.24	not det	not det	0.10	0.19	not det
SO <sub>3</sub> .....	0.17	0.12	0.82	1.88	1.11	2.86	0.17	0.12	1.71
P <sub>2</sub> O <sub>5</sub> .....	0.64	1.13	2.62	2.94	0.50	3.72	0.51	0.15	1.98
CO <sub>2</sub> .....	36.51	31.47	27.66	19.10	28.30	not det	33.88	33.15	25.50
	99.60	100.49	99.55	99.93	98.93		99.21	99.67	99.46

[CONTRIBUTIONS FROM THE CHEMICAL DIVISION OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 33.]

ON THE DETERMINATION OF POTASH WITHOUT THE PREVIOUS REMOVAL OF IRON, CALCIUM, ETC.

By C. C. MOORE.<sup>1</sup>

Received March 18, 1898.

I HAVE found it practicable to wash out ferric, aluminic and other chlorides, and the excess of platinic chloride which is present by means of an acidulated alcoholic wash. Thus it is possible to avoid the precipitation and filtering of ferric hydroxide, calcium oxalate, etc., and the subsequent evaporation and ignition for the removal of ammoniacal salts.

The substance under examination is brought into solution by the usual acid digestion, and the excess of acid removed by evaporation, the residue and insoluble matters separated by filtration. The filtrate is now ready for the potash estimation. To it is added the usual platinic chloride solution, only enough

<sup>1</sup> Communicated by Dr. H. W. Wiley.

to combine with the potash being necessary. The mixture is evaporated, on the steam-bath, nearly to dryness, so that it solidifies on cooling, just as in the ordinary determination. From fifteen to twenty-five cc. of the acidulated alcohol are added, and allowed to stand two or three minutes with an occasional stirring. The ferric, aluminic, etc., and excess of platinic chlorides readily go into solution, leaving the crystallized potassium chlorplatinic salt and part of the neutral sulphates, sodium chloride, etc. These residues are brought onto a filter, either paper or Gooch, and after one or two washings by decantation, the potassium chlorplatinic salt and the other residue are washed onto the filter, and washing continued with the same acidulated alcohol until all excess of platinic chloride is washed out. Now wash with the Lindo ammonium chloride solution (200 grams ammonium chloride to one liter of water) until sulphates, sodium chloride, etc., are washed out. Then wash out the ammonium chloride with eighty-five per cent. alcohol, after which a pure potassium chlorplatinic salt is left, which is dried and weighed as usual.

The acidulated alcohol is prepared by passing dry hydrochloric acid gas into cool ninety per cent. alcohol. This is easily done by gently heating strong aqueous hydrochloric acid in a flask. The liberated gas is passed through sulphuric acid, and into the alcohol which is kept in a cooled vessel. Some ethyl chloride will be formed, but most of the gas will be held in solution mechanically by the alcohol. The absorption is continued until one cc. of the alcohol neutralizes about two and one-third cc. of a normal potassium hydroxide solution, using phenolphthalein or any other suitable indicator.

The solvent action of this acidulated alcohol on potassium chlorplatinic salt is about equal to that of the Lindo ammonium chloride solution, and about one-third that of ordinary eighty per cent. alcohol. Or, if expressed in figures, one gram of pulverized potassium chlorplatinic salt was digested for two hours in 500 cc. of acidulated alcohol, at a room temperature of 80°, the flask being shaken continuously. The solvent action under these conditions was found to be one part in 60,000.

In experimenting, the ash sample used by the "Association of Official Agricultural Chemists" in 1897 was used. The reporter

found this ash to contain about 11.05 per cent. of potash. The sample was digested in hydrochloric acid, evaporated to dryness and taken up with hydrochloric acid and water, so that the portion of the filtrate used corresponded to one-half gram of ash, and contained less than one-half cc. of hydrochloric acid. Four portions were taken from each of two samples, and only sufficient platinic chloride was added to combine with the potassium chloride present. The variation of the maximum and minimum results in each sample was 0.03 per cent., and the average of the eight determinations varied 0.01 per cent. from the result found by the Association.

It was desired to see under what extreme conditions the potash could be determined. An aliquot portion corresponding to one-half gram was used. To this were added 2.0 grams ferric chloride, 0.30 gram aluminic chloride, 0.20 gram sodium chloride, and 0.03 gram calcium sulphate, and only sufficient platinic chloride to combine with the potassium chloride. The result was less than 0.40 per cent. higher than the known percentage, and it is possible that potash was in the chemicals added.

Again, a solution was made of 0.30 gram potassium chloride, 0.56 gram calcium sulphate, 1.00 gram sodium chloride, and 7.0 grams ferric chloride. Only five cc. of a standard solution of platinic chloride were added, which is but a trifle above the requisite amount for the potassium chloride. Duplicate determinations and a blank were run. The evaporation was continued until a solution of the consistency of molasses was formed amounting to about five cc. To wash each sample in a Gooch, 190 cc. of the acidulated alcohol, and 250 cc. of ammonium chloride solution were used, and thirty-five minutes required for complete washing.

While one sample recovered 110 per cent. of the original potassium chloride, the second result was 100.50 per cent., and the blank was not stained. The potassium chlorplatinate crystals were below medium size, very uniform and of splendid color.

It was observed that the presence of other salts was beneficial, as it made the crystallization of the potassium chlorplatinate more perfect, and prevented any subsequent reduction.

Should the original substance contain ammoniacal salts, they

must be removed, else ammonium chlorplatinate will be formed.

The decomposition and removal of ammoniacal salts by nitric acid is most applicable here. The process is described in "Crookes' Select Methods," page 32. If hydrochloric acid is present, it is beneficial, as the chlorine which would be liberated also decomposes ammoniacal salts.

### THE DETERMINATION OF METHANE, CARBON MONOXIDE, AND HYDROGEN BY EXPLOSION IN TECHNICAL GAS ANALYSIS.

BY W. A. NOYES AND J. W. SHEPHERD.

Received March 7, 1908.

THE determination of carbon monoxide in technical gas analysis with the Orsat apparatus is not very satisfactory, partly because the gas is absorbed so slowly by the cuprous chloride, and partly because the cuprous chloride must be very frequently changed unless two absorption bulbs filled with the reagent are used. These difficulties may be avoided and the carbon monoxide, hydrogen, methane, and nitrogen may be determined by explosion, if the determination is accompanied by a determination of the oxygen consumed in the combustion, by explosion, of a known volume of the gas. For this purpose we have introduced in the Orsat apparatus place of the fourth bulb an explosion pipette the form shown in Fig. 1. The pipette has the advantage over that usually supplied with apparatus for gas analysis, that during the explosion the gas is confined by glass stop-cocks on both sides, insuring positively against loss during the moment of high pressure in the apparatus. A little sulphuric acid is added both to the water in the explosion pipette and to that in the measuring burette. This greatly decreases the ionization of the carbonic acid and so lessens the solubility of the carbon dioxide in the water. The results given below demonstrate that the error arising from the solubility of carbon dioxide in dilute acid in the case of mixtures containing six to eight per cent. of the gas must be very small.

Fig. 1.

For the purpose of determining the amount of oxygen remaining after the explosion, we have attached to the outer end of the capillary tube of the Orsat apparatus a small hydrogen generator of the form shown in Fig. 2. The hydrogen is generated from

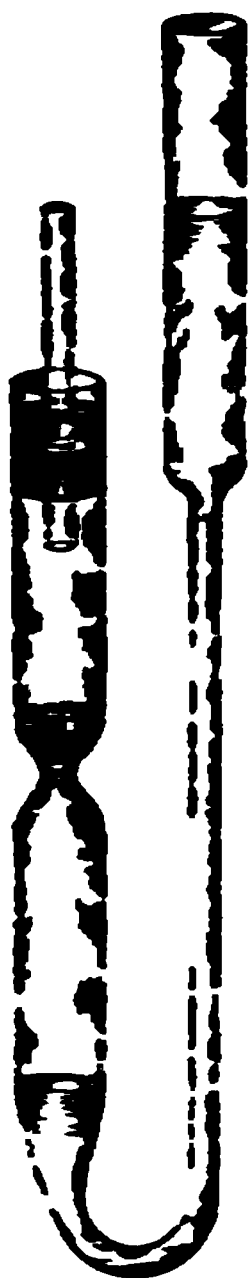


Fig. 2

aluminum foil and a solution of potassium hydroxide of sp. gr. 1.27. The lower bulb of the generator should have a capacity of about twenty cc. The stopper bearing the delivery-tube of the generator is pushed into its mouth and covered with water to avoid diffusion of the hydrogen, and the rubber connection with the capillary tube of the Orsat is surrounded with a glass tube filled with water for the same reason. With these precautions, hydrogen, which is almost chemically pure, may be taken into the measuring tube of the apparatus whenever desired.

The analysis is carried out as follows: In the case of illuminating gas the carbon dioxide is absorbed in potassium hydroxide of sp. gr. 1.27, the illuminants in fuming sulphuric acid followed by the caustic potash, and the oxygen in an alkaline solution of pyrogallol. The residue is then left over the pyrogallol, the side bottle is raised till all gas is expelled from the capillary tube of the apparatus, and then about eighty-five cc. of air are taken in and accurately measured. In all measurements three minutes were allowed for the water to run down the walls of the burette. The burette was kept at a constant temperature by running water through the jacket surrounding it, as the temperature of the room where we worked was quite variable. To facilitate accurate reading, a scale corresponding to the scale of the burette, was made on the edge of the case of the apparatus. By means of such a scale it is very easy to bring the water in the side bottle to the level of the water in the measuring tube and also to bring the eye to the exact level required. After measuring the air gas is admitted from the residue over the pyrogallol. The amount to be taken will vary, of course, with its character. It should be taken in such amount as to require nine to ten cc.

of oxygen for its complete combustion. If too much is taken, there may be danger of burning nitrogen, and also there will not be enough oxygen left for the second explosion with hydrogen. With a gas of unknown composition six to eight cc. may usually be taken at first and, if the mixture will not explode, hydrogen may be added, one cc. at a time, till an explosion can be secured. From the data thus secured the amount of the gas which should be used can be determined. Before attempting an explosion the gas should be passed into an explosion pipette and back to the measuring burette at least twice, and better three times, to secure thorough mixing. After the explosion the contraction is determined and then the carbon dioxide. Then about twenty cc. of hydrogen are added, and after mixture as before, and explosion, the contraction is determined. One-third of this contraction will give the amount of oxygen remaining after the first explosion. If this amount of oxygen be subtracted from the amount in the air originally taken, the difference will be the amount of oxygen used in the first explosion. Air is assumed to contain 20.9 per cent. of oxygen in these calculations.

The calculation of the results is based on the following equations, in which the symbols are used to represent volumes of gas :

1.  $\text{CH}_4 + \text{CO} + \text{H} + \text{N} = \text{Gas taken.}$
2.  $2\text{CH}_4 + \frac{1}{2}\text{CO} + \frac{3}{2}\text{H} = \text{Contraction.}$
3.  $2\text{CH}_4 + \frac{1}{2}\text{CO} + \frac{1}{2}\text{H} = \text{Oxygen consumed.}$
4.  $\text{CH}_4 + \text{CO} = \text{CO}_2 \text{ formed.}$

Hence

$$\begin{aligned} \text{H} &= \text{Contraction less oxygen consumed.} \\ \text{CO} &= \frac{2}{3}(2\text{CO}_2 + \frac{1}{2}\text{H} - \text{O consumed}). \\ \text{CH}_4 &= \text{CO}_2 - \text{CO.} \\ \text{N} &= \text{Total gas} - (\text{H} + \text{CO} + \text{CH}_4). \end{aligned}$$

The following is an illustration of the record of an analysis :

	Reading.	Volume.
Air .....	12.96	87.04
Gas .....	0.58	12.38
Contraction.....	15.4	14.82
CO <sub>2</sub> .....	23.39	7.99
H .....	1.24	22.15
Contraction.....	24.35	23.11
Oxygen originally present.....	....	18.19
“ of second explosion.....	....	7.71
“ of first explosion .....	....	10.48

Hence

	Per cent.
Hydrogen = 4.34 =	35.06
Carbon monoxide = 5.12 =	41.38
Methane = 2.87 =	23.19
	<hr/>
	12.33    99.63

To determine the accuracy of the method, a mixture of known composition was prepared. Hydrogen was first admitted into the measuring tube of the burette, from the generator described, and then methane, generated from sodium acetate and soda-lime, was introduced. After thorough mixture, three determinations of the proportion between the methane and hydrogen were made in the usual manner by explosion. The results agreed quite closely with the composition of the gas as determined by measurement, indicating that the methane was practically pure.<sup>1</sup> The results were :

	Calculated.	Found.			Average.
Methane .....	38.5	39.9	39.3	39.2	39.5
Hydrogen .....	61.5	60.0	60.0	60.7	60.2
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	99.9	99.3	99.7	99.7

	Calculated.	Found.			Average.
Methane .....	37.6	38.2	38.0	38.5	38.2
Hydrogen .....	62.4	60.9	61.3	60.2	60.8
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	99.1	99.3	98.7	99.0

There seems to be some tendency to high results for methane, but the close approximation to 100 for the total indicates that there was probably some loss of hydrogen by diffusion or absorption. If the gases are thoroughly mixed before explosion, there would seem to be no occasion for such gross errors in the determination of hydrogen as were observed by Gill and Hunt.<sup>2</sup> Gases mix by diffusion very much less quickly than is commonly supposed.

The remainder of the mixture of methane and hydrogen was then carefully measured and a mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with concen-

<sup>1</sup> This accords with the statement of Freyer and Meyer, *Zeit. phys. Chem.*, 11, 28, but not with that of Gill and Hunt in this Journal, 17, 958.

<sup>2</sup> This Journal, 17, 992.



trated sulphuric acid was added. After removal of the carbon dioxide, the gas was again measured, and, on the basis of the result, combined with the results of the analysis of methane and hydrogen, the composition of the total gas was calculated. A series of analyses of the mixture was then made.

FIRST SERIES.

	Calculated.	Found.					Average
Methane . . . . .	23.08	23.6	23.0	22.8	23.3	23.3	23.21
Carbon monoxide..	41.52	39.6	40.6	40.9	41.2	40.5	40.55
Hydrogen . . . . .	35.23	35.0	35.6	35.4	35.0	34.5	35.09
	<u>99.83</u>	<u>98.2</u>	<u>99.2</u>	<u>99.1</u>	<u>99.5</u>	<u>98.3</u>	<u>98.85</u>

SECOND SERIES.

	Calculated.	Found.						Average
Methane . . . . .	22.37	22.7	23.1	22.6	22.7	22.7	22.4	22.68
Carbon monoxide..	41.48	40.4	40.0	40.5	40.2	39.8	40.0	40.15
Hydrogen . . . . .	35.80	35.3	35.4	35.6	35.9	35.7	35.9	35.64
	<u>99.65</u>	<u>98.4</u>	<u>98.5</u>	<u>98.7</u>	<u>98.8</u>	<u>98.2</u>	<u>98.3</u>	<u>98.47</u>

The objection that the error is multiplied because of the small amount of gas which must be taken for the explosion, applies to this method as it does to the usual explosion method for methane and hydrogen, of course. It is to be noticed, however, that the determination of methane, the most valuable constituent as a fuel, depends on the combined measurements of the carbon dioxide, the contraction, and the oxygen consumed, instead of depending on the carbon dioxide alone, as is the case with the older method. By the method in common use any carbon monoxide which has failed of absorption is counted as methane after the explosion. Another advantage is that the errors are of a compensating nature, so that when methane is found too high, carbon monoxide and hydrogen will usually be found low, and in such ratio that the total fuel value will be nearly constant.

We have used with the Orsat apparatus a stop-cock lubricant described by Professor Ramsay at the Toronto meeting of the British Association, though he said it was not original with him. Equal parts of black rubber, vaseline, and paraffin are heated to gentle boiling for a quarter of an hour in a beaker. The lubricant is sufficiently viscous to hold against an atmosphere of pressure, if necessary, gives no hydrocarbon vapor to a vacuum, and

the stop-cocks in which it is used do not become set even after long standing. The last property makes it especially valuable for the Orsat apparatus.

ROSE POLYTECHNIC INSTITUTE.

## PROTEIDS OF THE PEA.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

IN a paper on the "Proteids of the Pea and Vetch"<sup>2</sup> the legumin obtained from these seeds was described and some account was also given of other accompanying proteids. Further study has furnished much additional information concerning these substances and made necessary a review of our former work on the pea and vetch.

On investigating the proteid constituents of the horse bean and lentil we found that by repeated fractional precipitations, the globulin from these seeds was separated into fractions, on the one hand wholly free from coagulable matter and on the other consisting of substance which was substantially all coagulable. The former we found to be legumin, in all respects like that described by us from the vetch, and the latter to be a new proteid of different composition and properties, to which we have given the name *vicilin* since we first recognized its presence in the horse bean (*vicia faba*).

This discovery led us to reinvestigate the proteids of the pea and we thus found that the legumin of that seed, as formerly described by us, was contaminated with more or less vicilin and that when the latter is completely separated the differences noted in our former paper between the legumin of the pea and that of the vetch disappear and preparations from these two seeds are identical in composition and reactions.

Leguminous seeds contain about one and two-tenths per cent. of alkali and one per cent. of phosphoric acid, while in the seeds of the cereals but five-tenths and seven-tenths per cent. of these substances respectively are present.

Liebig and Rochleder as well as Ritthausen attributed the

<sup>1</sup> Reprinted from advance sheets of the report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

<sup>2</sup> This Journal, 18, 583; Report of the Connecticut Agricultural Experiment Station for 1895.

presence of much legumin in the aqueous extracts of leguminous seeds to the basic alkali phosphates. But the water extracts are strongly acid to litmus and accordingly must contain acid phosphates.

We find that a mixture of hydrogen potassium phosphate with enough phosphoric acid to be distinctly acid to litmus, but strongly alkaline to lacmoid, freely dissolves legumin to solutions that behave in all respects like the aqueous extracts of these seeds. Such solutions are unlike those obtained with neutral salts, not being easily precipitated by dilution unless holding a very large proportion of proteid. They yield precipitates with acetic acid which are wholly soluble in sodium chloride brine, thus resembling solutions in sodium bicarbonate.

In this and the following papers we give the results of our investigation upon each seed, and in the last paper, a general summary of the properties and composition of the different proteids which we have found.

Finely ground meal of garden peas was prepared in the laboratory almost entirely free from the outer coating of the seed. Immediately after grinding, 1,800 grams were treated with a large quantity of ten per cent. salt solution, strained through fine bolting-cloth and, after standing three hours to deposit insoluble matter, the turbid extract was siphoned off and saturated with ammonium sulphate. The precipitate was filtered out, suspended in a little water and dialyzed for eighteen hours. A large part of the ammonium sulphate was thus removed and the proteid dissolved by the dilute saline solution which remained. This solution was filtered perfectly clear through a thick felt of paper pulp and dialyzed for four days. A large precipitate resulted from which, after settling, the solution, A was decanted and treated as described on page 353; the precipitate was dissolved in about 1500 cc. of ten per cent. brine, the solution filtered clear and made exactly neutral to litmus paper by the cautious addition of seventy-five cc. of two-tenths per cent. potash water. The solution was then dialyzed for forty hours, whereby globulin separated out in well-defined spheroids which, after settling, united to a coherent mass exactly like vetch legumin, and differing from our previously described pea legumin that had formerly been obtained as a pulverulent pre-

cipitate. A portion of this precipitate was washed thoroughly with water and with alcohol and dried over sulphuric acid, giving 16.83 grams of preparation 32, which had, after drying at 110°, the following composition :

GLOBULIN, 32. <sup>1</sup>	
Carbon .....	51.87
Hydrogen .....	7.01
Nitrogen .....	17.69
Sulphur.....	0.40
Oxygen .....	23.03
	<hr/>
	100.00
Ash .....	0.62

This preparation, unlike those made from unneutralized solutions, was almost free from substances insoluble in salt solution. Dissolved in ten per cent. brine and heated above 90°, turbidity was produced, which at 98°-100° developed slowly into a considerable coagulum.

During the washing of this preparation considerable substance dissolved in water, yielding a solution which was perfectly neutral to litmus (indicating the absence of acid globulin), and which on adding a little salt, gave a precipitate that with more salt dissolved completely to a solution coagulable by heating.

The remainder of the proteid, of which 32 was a part, was dissolved by adding fifty cc. of ten per cent. salt solution and the resulting liquid was diluted with water until it contained about 1.25 per cent. of salt. A large part of the proteid was thus thrown down and settled out as a viscid layer, from which after an hour the supernatant fluid was almost completely decanted. This deposit, X, was then washed with 200 cc. of water, which caused it to become opaque and pasty. The wash-water, after decanting, was added to the solution from which the proteid had separated, and thereupon another precipitate, Y, resulted, from which, after settling, the solution was decanted and dialyzed, thereby yielding precipitate Z.

As precipitate X was found to give a decided turbidity on heating its solution in a boiling water-bath, it was dissolved by add-

<sup>1</sup> To avoid confusion and facilitate reference the preparations described in this paper are numbered consecutively with those given in the paper on "Legumin and other Proteids of the Pea and Vetch," this Journal, 18, 583.

ing ten grams of sodium chloride and water enough to make a final volume of 350 cc. The clear solution which resulted, containing about three per cent. of salt, was diluted with water until it contained about one and three-fourths per cent. of salt. A large precipitate, I, separated, which rapidly settled as a viscid, semi-fluid layer from which the solution II was soon completely decanted. As the precipitate I, when dissolved in salt solution, still gave a slight turbidity on heating to 99°, it was washed with water, dissolved in 100 cc. of ten per cent. salt solution, and reprecipitated by diluting the resulting clear liquid with 900 cc. of water. The precipitate which separated was now found to be wholly free from any coagulable matter, for not the slightest turbidity was produced in its solutions in brine even by prolonged heating in a boiling water-bath. The substance was therefore washed thoroughly with water and with alcohol and dried over sulphuric acid, thus giving 12.33 grams of preparation 33, which had, when dried at 110°, the following composition :

LEGUMIN, 33.

Carbon .....	51.74
Hydrogen .....	6.90
Nitrogen .....	18.04
Sulphur.....	0.42
Oxygen .....	22.90
	<hr/>
	100.00
Ash .....	0.78

The solution decanted from 33 was dialyzed free from chlorides and a precipitate obtained which when washed and dried in the usual manner weighed 4.44 grams and had the composition shown by the following figures :

GLOBULIN, 34.

Carbon .....	52.06
Hydrogen .....	6.99
Nitrogen .....	17.86
Sulphur.....	0.36
Oxygen .....	22.73
	<hr/>
	100.00
Ash .....	0.32

Solution II, page 351, was next diluted with an equal volume of water until it contained about nine-tenths per cent. of salt ; after standing a short time the solution was decanted and the liquid precipitate washed thoroughly with water and alcohol and dried, giving 6.47 grams of preparation 35.

GLOBULIN, 35.

Carbon .....	51.95
Hydrogen .....	0.96
Nitrogen .....	17.76
Sulphur .....	0.42
Oxygen .....	22.91
	<hr/>
	100.00
Ash .....	0.57

The filtrate from 35 was dialyzed free from chlorides and yielded 5.18 grams of preparation 36, which after the usual treatment gave on analysis the following results :

GLOBULIN, 36.

Carbon .....	52.43
Hydrogen .....	7.04
Nitrogen .....	17.45
Sulphur .....	0.23
Oxygen .....	22.85
	<hr/>
	100.00
Ash .....	0.40

Preparations Y and Z obtained as successive precipitates from the solution decanted from X, as described on page 350, were separately washed with water and alcohol and dried over sulphuric acid, giving respectively preparation 37, weighing 8.06 grams, and preparation 38, weighing 6.80 grams. These had the composition given below :

GLOBULIN.

	37	38
Carbon .....	52.08	52.20
Hydrogen .....	6.90	7.01
Nitrogen ....	17.65	17.53
Sulphur .....	0.28	0.15
Oxygen .....	23.09	23.11
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.75	0.46

The solution, described on page 349, that had been decanted from the mixed globulin and after forty hours' dialysis had yielded the preparations 32-38, was further dialyzed for four days and 11.2 grams of globulin obtained having, when dried at 110°, the following composition :

GLOBULIN, 39:

Carbon .....	52.45
Hydrogen .....	7.04
Nitrogen .....	17.22
Sulphur.....	0.16
Oxygen .....	23.13
	<hr/>
	100.00
Ash .....	0.18

It will be noticed that by this extensive fractional precipitation of the pea globulin, a separation was effected which yielded legumin, agreeing in reactions with that of the vetch as formerly described, and with that of the lentil and horse bean, as will be shown later in this paper, and vicilin, a more soluble globulin of somewhat different composition, which is coagulated by heating its solutions to about 95° and has a very remarkably low content of sulphur. The composition of vicilin is shown by the analyses 36, 38 and 39, which represent the most soluble globulin contained in the solutions from which they were separated.

VICILIN.

	36	38	39
Carbon.....	52.43	52.20	52.45
Hydrogen.....	7.04	7.01	7.04
Nitrogen.....	17.45	17.53	17.22
Sulphur .....	0.23	0.15	0.16
Oxygen.....	22.85	23.11	23.13
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

The reactions of legumin and vicilin will be given fully in a following paper after describing the preparation of these proteids from other legumes.

On page 349 we described how, after dialyzing for four days, the solution of the precipitate obtained by saturating the seed extract with ammonium sulphate, the greater part of the glob-

ulin was precipitated, and stated that the solution filtered from this globulin, there marked A, was reserved for further notice. This solution, which by dialysis had become bulky, was saturated with ammonium sulphate and the precipitate produced, filtered out, suspended in a little water and dialyzed over night. In this way the proteids were concentrated in a small volume of liquid. This solution was then filtered clear and dialyzed. After five days the precipitate which had separated was filtered out and extracted with ten per cent. salt solution, but as only very little dissolved, it was washed free from chlorides with water, then with alcohol and dried at 110°. Analysis showed it to have the following composition :

LEGUMELIN, 40.	
Carbon.....	52.93
Hydrogen .....	7.10
Nitrogen .....	16.18
Sulphur.....	0.85
Oxygen .....	22.94
	<hr/>
	100.00
Ash .....	0.22

The filtrate from 40 was then saturated with ammonium sulphate and the precipitate produced, dissolved in as small a volume of water as possible, filtered clear and dialyzed seven days. A very slight precipitate separated which was filtered out, washed thoroughly with water and found to dissolve in ten per cent. brine, giving a solution which yielded a flocculent coagulum at 53°; the heat coagulation point of the body we designate *legumelin*. The solution from which this small precipitate had separated, after filtering, was heated in a water-bath to 67° and a large coagulum produced which was washed thoroughly with hot water and then with alcohol and dried over sulphuric acid, giving eighteen grams of 41.

The filtrate from 41 was heated to 95° and the resulting coagulum, washed and dried, formed preparation 42, weighing 4.10 grams. Dried at 110° these gave the following results when analyzed :



LEGUMELIN.

	41	42
Carbon .....	53.24	53.36
Hydrogen .....	6.99	6.98
Nitrogen .....	16.15	16.24
Sulphur .....	1.09	1.01
Oxygen.....	22.53	22.41
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.21	0.21

Another extract, obtained in substantially the same manner as that just described, after removing most of the globulin by dialysis, was saturated with ammonium sulphate and the precipitate produced was dissolved in a little water and its solution dialyzed for seven days, giving a precipitate which was filtered out and found to consist almost wholly of proteid matter insoluble in salt solution. After extracting with brine, this substance was thoroughly washed with water and dried, giving 4.24 grams of preparation 43. The filtrate from 43 was dialyzed in pipe water for five days longer, but as no more precipitate resulted, it was dialyzed for five days in a large volume of distilled water, which was frequently changed and kept cool by adding ice containing only an extremely small quantity of mineral matter. No precipitate was thus separated, and to the solution was then added ten per cent. of sodium chloride and acetic acid as long as a precipitate formed. The resulting precipitate was filtered out, dissolved in water and sodium carbonate added to very slight alkaline reaction. This caused a large precipitate which when prepared for analysis weighed 5.73 grams, preparation 44. The solution filtered from this neutralization precipitate, contained only a very little proteid, as shown by saturating the filtrate with ammonium sulphate.

The filtrate from the precipitate produced by acetic acid in the ten per cent. salt solution was unchanged on further addition of acetic acid and was therefore saturated with sodium chloride which gave a second precipitate. This was filtered out, dissolved in water, the solution filtered clear and dialyzed. After chlorides had diffused away the solution was perfectly neutral to litmus and quite clear. It was accordingly concentrated by dialysis in alcohol and the precipitated proteid, 45, dehydrated

by absolute alcohol, and dried, weighed 5.87 grams. These preparations were analyzed with the following results :

LEGUMELIN.			
	43	44	45
Carbon .....	53.03	53.43	53.23
Hydrogen.....	7.10	7.01	6.91
Nitrogen.....	16.30	16.50	16.08
Sulphur .....	1.01	1.16	1.11
Oxygen .....	22.56	21.90	22.67
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Ash.....	0.35	0.80	0.56

It will soon be shown that the proteose of the pea is precipitated by acetic acid from a solution saturated with sodium chloride, and it might be expected that 45 would therefore contain a large proportion of proteose; but as it was found that this preparation through washing with alcohol and drying at 110° had become insoluble in water, it is probable that the proteose had mostly diffused away during the long dialysis to which the solutions had been subjected.

If the last six analyses are compared, it will be seen that they are in close agreement except 40, in which carbon and sulphur are somewhat lower, due we think to the preseuce of a little vicilin which might be expected to be present, owing to the method of preparation. To facilitate comparison the other five analyses are arranged in the following table together with those of 5 and 8 described in our former paper.

LEGUMELIN.								
	5	8	41	42	43	44	45	Aver.
Carbon .....	53.33	53.54	53.24	53.36	53.03	53.43	53.23	53.31
Hydrogen ..	6.98	6.99	6.99	6.98	7.10	7.01	6.91	6.99
Nitrogen ....	16.14	16.69	16.15	16.24	16.30	16.50	16.08	16.30
Sulphur.....	1.00	1.01	1.09	1.01	1.01	1.16	1.11	1.06
Oxygen .....	22.55	21.77	22.53	22.41	22.56	21.90	22.75	22.34
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

- 5 and 8, coagulated by alcohol.
- 41, coagulated by heat at 67°.
- 42, coagulated by heat at 95°.
- 43, coagulated by dialysis in water.

44, precipitated by acetic acid from ten per cent. salt solution.

45, precipitated by acetic acid from saturated salt solution.

The properties and reactions of legumelin will be discussed later after describing its occurrence in other seeds.

Returning to the first extract, the filtrate from 42 contained nothing coagulable on boiling. It was therefore dialyzed in alcohol and so concentrated to small volume. A quantity of proteid was thus precipitated which was filtered out and washed with absolute alcohol. The substance thus obtained, weighing 10.5 grams after drying over sulphuric acid, was dissolved in 100 cc. of water, with which it gave a clear solution, and sodium chloride was added to saturation, which caused a slight precipitate. This was filtered out, but owing to its small amount was not further examined. The filtered solution was then treated with salt-saturated acetic acid as long as a precipitate was produced, which required a relatively large amount of acid. The resulting gummy precipitate was washed with saturated salt solution, dissolved in water, the solution neutralized with a little sodium carbonate and dialyzed till free from chlorides, when the dialyzer was transferred to alcohol and the solution concentrated to small volume. The substance thus precipitated was filtered out, extracted thoroughly with absolute alcohol and dried over sulphuric acid giving 4.06 grams of preparation 46, having, when dried at 110°, the composition here given.

PROTEOSE, 46.

Carbon .....	50.24
Hydrogen .....	6.96
Nitrogen .....	17.35
Sulphur.....	1.25
Oxygen .....	24.40
	<hr/>
	100.00
Ash .....	0.92

The solution, filtered from 46, which had been thrown down by the addition of acetic acid to the solution saturated with salt, was neutralized with sodium carbonate, of which a large quantity was required, showing that only a small proportion of the acid had been precipitated with the proteose. This neutralized solution was dialyzed in water until free from chlorides and then con-

centrated by dialysis in alcohol. The substance thus precipitated was filtered out, washed with absolute alcohol, dried and found to weigh 1.76 grams. This, dried at  $110^{\circ}$ , gave the following results when analyzed :

PROTEOSE, 47.

Carbon.....	49.66
Hydrogen .....	6.78
Nitrogen .....	16.57
Sulphur.....	1.40
Oxygen .....	25.59
	<hr/>
	100.00
Ash .....	3.20

Preparations 46 and 47 give precipitates with copper sulphate which yield the usual rose-red biuret reaction on adding potash. With nitric acid they give no precipitates but yield yellow solutions on warming. If the solution is first saturated with salt, 46 gives a heavy precipitate with nitric acid which largely dissolves on heating and reprecipitates on cooling, while 47 under like conditions gives only a turbidity diminished by adding an excess of acid.

We have then in the pea the following proteids :

*Legumin*, a globulin not coagulated by heating its solutions.

LEGUMIN.

Carbon .....	51.74 <sup>1</sup>
Hydrogen .....	6.90
Nitrogen.....	18.04
Sulphur .....	0.42
Oxygen.....	22.90
	<hr/>
	100.00

*Vicilin*, a globulin soluble in a more dilute brine than legumin, coagulated on heating its solutions to  $95^{\circ}$ – $100^{\circ}$  and having the following composition :

VICILIN.

Carbon .....	52.36
Hydrogen .....	7.03
Nitrogen .....	17.40
Sulphur.....	0.18
Oxygen .....	23.03
	<hr/>
	100.00

<sup>1</sup> This figure for carbon is about four-tenths per cent. lower than that given in our former paper, a difference which we attribute to the fact that this preparation was made from a neutralized solution and that vicilin had been separated from it completely.

*Legumelin*, a proteid partially precipitated by dialysis, generally in a coagulated state, the greater part however remaining in solution even after prolonged dialysis. Whether it should be called a globulin or an albumin is perhaps questionable, but its relations seem to be closer to the albumins than to the globulins. Its composition as shown by the average of the analyses of five preparations obtained by three different methods, is :

LEGUMELIN.

Carbon .....	53.31
Hydrogen .....	6.99
Nitrogen .....	16.29
Sulphur.....	1.06
Oxygen .....	22.35
	<hr/>
	100.00

A *Protoproteose* precipitated by acetic acid from its solution saturated with salt :

PROTOPROTEOSE.

Carbon .....	50.24
Hydrogen .....	6.76
Nitrogen .....	17.35
Sulphur.....	1.25
Oxygen .....	24.40
	<hr/>
	100.00

A *deuteroproteose* not precipitated by acetic acid from the salt saturated solution :

DEUTEROPROTEOSE.

Carbon .....	49.66
Hydrogen .....	6.78
Nitrogen .....	16.57
Sulphur.....	1.40
Oxygen .....	25.59
	<hr/>
	100.00

The combined amount of legumin and vicilin which we have obtained by dialyzing extracts of the pea was about ten per cent., as the following experiments show.

Of the finely ground pea meal, 200 grams were treated with one liter of water, the mixture poured on a coarse sieve and the

lumps broken up and washed through with another liter of water. After standing over night, in a cool place, protected with thymol, the suspended matters settled leaving a somewhat turbid solution, of which 1500 cc. were siphoned off and filtered on a pulp filter. The first 300 cc. which passed through the filter were rejected, as they were mixed with the water contained in the pulp. The next liter of clear solution was dialyzed until all that could be thus precipitated had separated in the form of minute spheroids. In this way there was obtained a quantity of proteid which weighed 4.35 grams when washed with alcohol and dried over sulphuric acid. The extract from which this was separated was one-half the total and therefore corresponded quite nearly to that yielded by 100 grams of meal, thus showing that 4.35 per cent. thereof was extracted by distilled water and precipitated by dialysis.

The meal residue (from which, as described, three-fourths of the extract had been siphoned), together with the still adhering one-fourth of the extract, was treated with ten per cent. salt solution until the volume was 2000 cc. After settling, the solution was siphoned off, filtered perfectly clear, and dialyzed until all the globulin was precipitated. In this way 9.83 grams of globulin were obtained. As the meal residue before this extraction contained one-fourth of the water extract there should have been present 2.18 grams of proteid soluble in water and precipitable by dialysis. As three-fourths of the total salt extract yielded the above 9.83 grams there should be deducted therefrom three-fourths of 2.18 grams or 1.64 grams, making 8.19 grams of globulin obtained from three-fourths of 200 grams of meal or 5.46 per cent. which added to 4.35 per cent. makes 9.81 per cent. total globulin.

To another lot of 100 grams of meal 500 cc. of water were added, containing just enough baryta to produce an extract reacting neutral to litmus and to this 500 cc. of ten per cent. salt solution were added. From 750 cc. of this extract filtered clear, 7.33 grams of globulin separated on dialysis, equal to 9.77 per cent. of the meal. In another experiment, carried out in essentially the same manner, 10.0 per cent. of globulin was obtained.

By treating the residual meal with alkali but very little more proteid was dissolved. On digesting pea meal with ten times its

weight of one-tenth per cent. soda solution, a gelatinous mass resulted from which no clear extract could be obtained. If however a baryta solution of equal molecular strength was used the extract was readily filtered. From such an extract, filtered perfectly clear, there was obtained by adding acetic acid in slight excess 10.56 per cent. of proteid and by dialyzing the filtrate therefrom 3.16 per cent. more. Whether this 13.72 per cent. of proteid was substantially all legumin and vicilin we have no means of knowing. In the first of these experiments it will be noticed that 4.35 per cent. of globulin was obtained by dialyzing the aqueous extract. As the water used in this extraction weighed ten times as much as the meal the saline solution resulting from the mineral constituents of the seed would be so exceedingly dilute as to make it seem doubtful that so much globulin could be thereby dissolved. The reactions of this extract were therefore studied with a view to determine if possible the cause of the solution of the proteid.

When the extract was cautiously poured into distilled water a faint cloud formed at the point of contact of the two liquids which wholly disappeared on shaking. Under similar conditions a globulin solution commonly gives a permanent turbidity. Sodium chloride carefully and very gradually added, beginning with a minute quantity, gave no trace of a precipitate until the solution was saturated with the salt, when a very little proteid separated. A little acetic acid gave a precipitate completely dissolving on adding sodium chloride. If however a somewhat greater quantity of acid was added the precipitate did not wholly dissolve. By cautiously adding very dilute sodium carbonate solution even up to strong alkaline reaction no trace of a precipitate was observed.

Baryta solution when added in considerable quantity gave a little precipitate, probably due to phosphates. Calcium chloride gave a slight precipitate soluble in an excess of calcium or sodium chlorides. Calcium sulphate gave no precipitate.

From this it will be seen that solution of the globulin is apparently not due to the presence of acids, for neutralization gives not even a turbidity, nor to the presence of neutral salts since dilution does not give a permanent precipitate.

An extraction, with water containing just enough baryta to

leave the solution neutral to litmus, was made exactly like that described. This gave 3.75 per cent. of globulin on dialysis as against 4.35 per cent. extracted with water alone. By heating the filtrate from the above-mentioned preparation to 85° and washing and drying the coagulum, the amount of legumelin was found to be 2.03 per cent. of the meal.

### PROTEIDS OF THE LENTIL.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 20, 1898.

THE proteid substance of the lentil was first observed by Einhof in 1806<sup>2</sup>. Liebig<sup>3</sup> stated that plant-casein is obtained from beans, lentils, and peas. Dumas and Cahours<sup>4</sup> extracted lentils with warm water, allowed the extract to deposit suspended impurities and precipitated the proteid from the decanted solution by adding acetic acid. After washing the substance thus separated with water and alcohol and drying it, they obtained the following figures by analysis :

Carbon .....	50.46
Hydrogen .....	6.65
Nitrogen .....	18.19
Oxygen, etc. ....	24.70
	<hr/>
	100.00

Ritthausen<sup>5</sup> described a single preparation of proteid from this seed, obtained in nearly the same way as the preceding, for which he gave the following composition :

Carbon .....	52.53
Hydrogen .....	6.84
Nitrogen .....	16.49
Sulphur .....	0.40
Oxygen .....	23.74
	<hr/>
	100.00

For our work, coarsely ground lentils were freed almost completely from the outer seed coats by a current of air and were then

<sup>1</sup> Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

<sup>2</sup> Gehlen's *J. der Chem.*, 6, 543.

<sup>3</sup> *Ann. Chem. Pharm.*, 39, 138.

<sup>4</sup> *J. prakt. Chem.*, 28, 398.

<sup>5</sup> *Die Eiweisskörper*, etc., Bonn, 1872.



ground to a fine flour. Two kilograms of this flour were treated with ten liters of ten per cent. sodium chloride solution and after a short time the extract was strained out on fine bolting-cloth and allowed to stand over night in a cold place to deposit the suspended starch. The partly clarified extract was then passed through a centrifugal separator and finally filtered perfectly clear through a thick bed of filter-paper pulp. The extract was saturated with ammonium sulphate, the precipitate produced dissolved in dilute brine, the solution filtered perfectly clear and dialyzed for three days.

The globulin that had separated on dialysis was filtered out and, after washing with water and alcohol, dried over sulphuric acid. Preparation<sup>1</sup> 48 was thus obtained, which weighed 170 grams.

The solution from which 48 had separated was dialyzed for six days longer when it was filtered from a very small precipitate which, when washed and dried, formed preparation 49 that weighed 2.12 grams. The filtrate from 49 was saturated with ammonium sulphate, the separated proteid filtered out, dissolved in water, the solution filtered clear, and dialyzed. After prolonged dialysis but a trace of substance separated, which was filtered out, and the clear solution dialyzed in alcohol until all the proteid was precipitated. The substance thus obtained after drying weighed 6.78 grams. It was ground fine, exhausted with water and washed with alcohol, forming preparation 50.

These preparations were dried at 110° to constant weight and analyzed with the following results:

	48 <sup>1</sup>	49	50
Carbon .....	51.59	52.12	53.31
Hydrogen .....	6.99	6.88	6.71
Nitrogen.....	17.63	16.21	16.08
Sulphur .....	0.56	0.79	0.97
Oxygen.....	23.23	24.00	22.93
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Ash .....	0.49	0.79	0.74
Amount .....	170.0 grams	2.12 grams	6.78 grams.

<sup>1</sup> Numbered consecutively with the preparations of the proteids of the pea. This Journal, 19, 494.

In order to subject 48 to fractional precipitation one hundred grams were treated with 250 cc. of water and 250 cc. of ten per cent. brine added. A large part failed to dissolve, having been converted into an insoluble form by the process of separation. This part was collected on filters, washed with cold five per cent. brine, and then with hot brine of the same strength, the cold and hot washings being kept separate. The residue was next washed with water and with alcohol and dried, giving 62.23 grams of preparation 51. The washings made with hot brine were diluted with four volumes of water so as to form a one per cent. salt solution and the precipitate produced allowed to settle, when the solution was decanted and the deposit washed with water and alcohol and dried, yielding preparation 52, weighing 3.28 grams.

The solution filtered from 51, which measured 300 cc., was mixed with the cold washings, and diluted until the solution contained two per cent. of salt. The rapidly settling precipitate which separated was washed with water and with alcohol, and when dried weighed 4.75 grams, preparation 53.

The solution decanted from 53 was treated with an equal volume of water making a one per cent. brine, whereby substance was separated which, when washed and dried in the usual way, gave 9.5 grams of preparation 54.

The filtrate from 54 was cooled during the night to about 5° which caused a further deposit, that by the usual treatment gave 7.69 grams of preparation 55.

So large a proportion of 48 had become insoluble in salt solution, that it was thought best to make another lot of the globulin, which if possible should be more soluble. Accordingly 1000 grams of lentil flour were extracted with ten per cent. brine and the globulin separated by dialysis in exactly the same way as employed in making 48. Instead, however, of washing the substance on the filter with alcohol it was removed from the paper, redissolved in five per cent. brine, and the filters washed with the same solution. The filtrate and washings measured 800 cc. As 600 cc. of five per cent. brine had been used this solution contained thirty grams of salt. To this was added one liter of water, so that the resulting mixture contained 1.66 per cent. of sodium chloride and had a temperature of 25°. The large pre-

cipitate that appeared, soon settled to a coherent layer on the bottom of the jar, so that the solution, very nearly clear, could be decanted almost completely. The deposit was thoroughly washed with water and with alcohol, and after drying weighed 21.43 grams, preparation 56.

The solution decanted from 56 was cooled over night to 5°. The proteid separated as a dense semitransparent deposit which on washing with water became opaque and white. It was then dehydrated with absolute alcohol and dried, giving 16.10 grams of preparation 57.

The filtrate from 57 was dialyzed for four days whereby chlorides were completely separated. A coherent layer of globulin, which was deposited on the bottom of the parchment bag, when washed and dried weighed 32.8 grams and formed preparation 58.

These preparations were dried to constant weight and analyzed with the following results :

	GLOBULIN.							
	51	52	53	54	55	56	57	58
Carbon .....	51.52	51.43	51.44	51.62	52.13	51.53	51.39	52.05
Hydrogen ....	6.96	6.91	6.96	7.01	7.19	6.86	6.98	7.02
Nitrogen .....	17.69	18.02	17.99	17.87	17.47	18.06	18.03	17.29
Sulphur .....	0.50	23.64	0.44	0.46	0.23	0.49	0.44	0.21
Oxygen .....	23.33		23.17	23.04	22.98	23.06	23.16	23.43
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Ash .....	0.94	0.61	1.43	0.33	0.29	0.61	0.14	0.08

In this seed, as in the pea, we thus found that by fractional precipitation, the globulin is separated into two parts which differ in composition and solubility. As however none of the less soluble fractions was wholly free from coagulable matter, another extraction was made in which the acid of the seed was neutralized and the fractional precipitations were repeated until products wholly free from coagulable proteid were obtained.

Accordingly 2000 grams of meal were treated with ten liters of ten per cent. salt solution in which had been dissolved sufficient potash to yield an extract neutral to litmus, as determined by a preliminary trial. After thoroughly mixing, the whole was allowed to stand over night, with thymol, in a cool place, when the partly cleared extract was siphoned off and filtered. The solution was then saturated with ammonium sulphate, the pre-

precipitate filtered out, suspended in water and dialyzed over night. The proteid was thus dissolved, the solution filtered perfectly clear and dialyzed in two parts. Part I, which was obtained first, was treated as follows :

After dialyzing four days the precipitated globulin was filtered out and the filtrate A treated as subsequently described. The precipitate was dissolved in 500 cc. of two per cent. salt solution and 500 cc. of water added. A large precipitate formed, from which, after settling, the solution B was decanted.

The precipitate was then dissolved in 400 cc. of two per cent. salt solution and precipitated again by adding 400 cc. of water. The solution C was decanted from the precipitate thus thrown down, and the latter dissolved in five per cent. salt solution, and found to yield a considerable coagulum on heating in a boiling water-bath, showing it to still contain some vicilin. This latter solution was filtered clear and dialyzed for three days, when the precipitate which had formed was dissolved in 300 cc. of two per cent. salt solution, and 100 cc. of water added, causing a large precipitate which was found to be entirely free from coagulable matter. After washing this with water and alcohol, and drying over sulphuric acid, 23.67 grams of preparation 59 were obtained having the following composition when dried at  $110^{\circ}$  :

#### LEGUMIN 59.

Carbon .....	51.80
Hydrogen .....	6.86
Nitrogen .....	18.09
Sulphur.....	0.42
Oxygen .....	22.83
	<hr/>
	100.00
Ash .....	0.29

The solution decanted from 59 was treated with 200 cc. of water and the precipitate produced allowed to settle. The solution was then decanted and the precipitate washed with water and alcohol giving 5.36 grams of preparation 60, which, when dried at  $110^{\circ}$  and analyzed, gave the following results :

GLOBULIN, 60.

Carbon .....	51.83
Hydrogen .....	7.01
Nitrogen .....	17.75
Sulphur. ....	0.29
Oxygen .....	23.12
	<hr/>
	100.00
Ash .....	0.46

The solution decanted from 60 was dialyzed free from chlorides and the precipitate thereby separated, after washing and drying as usual, gave preparation 61, which analysis showed to contain :

VICILIN, 61.

Carbon .....	52.13
Hydrogen . ....	6.95
Nitrogen . ....	17.40
Sulphur.....	0.22
Oxygen .....	23.30
	<hr/>
	100.00
Ash .....	0.21

Solution B, page 366, was diluted with an equal volume of water which caused a precipitate, from which, after settling, the solution was decanted. This was washed, dried, and analyzed with the following results :

VICILIN, 62.

Carbon .....	52.28
Hydrogen .....	7.02
Nitrogen .....	17.41
Sulphur.....	0.08
Oxygen .....	23.21
	<hr/>
	100.00
Ash .....	0.21

The filtrate from this preparation was saturated with ammonium sulphate, but very little proteid was found in it.

Solution C, page 366, was also treated with an equal volume of water which precipitated a further quantity of globulin, that, when dried, weighed 5.55 grams, and had the following composition :

## VICILIN, 63.

Carbon .....	52.14
Hydrogen .....	7.02
Nitrogen .....	17.27
Sulphur.....	0.18
Oxygen .....	23.39
	<hr/>
	100.00
Ash .....	0.21

Solution A, described on page 366, from which the greater part of the globulin extracted from the meal, had been removed by dialysis, was saturated with ammonium sulphate. The precipitate produced was suspended in water and dialyzed over night, thereby bringing the proteid into solution in a comparatively small volume of water. This solution was then filtered perfectly clear, and dialyzed forty hours, when a considerable precipitate separated which was filtered out, washed, dried, and analyzed with results as follows :

## VICILIN, 64.

Carbon .....	52.03
Hydrogen .....	6.91
Nitrogen .....	17.60
Sulphur.....	0.13
Oxygen .....	23.33
	<hr/>
	100.00
Ash .....	0.26

The filtrate from 64, after uniting with the similar solution from part II of this extract, was further dialyzed for nine days, until free from sulphates, when the precipitate which had formed was filtered out, washed, dried, and analyzed ; It weighed only 1.13 grams and had the following composition :

## LEGUMELIN, 65.

Carbon .....	53.02
Hydrogen .....	—
Nitrogen .....	16.36
Sulphur }	—
Oxygen }	—
Ash .....	0.47

The clear solution filtered from 65 was then heated in a water-bath for three hours at 65° and the resulting coagulum filtered

out and the filtrate further heated to 82°, whereby a second coagulum was produced. These two preparations, 66 and 67 respectively, were washed with hot water and with absolute alcohol and gave on analysis, when dried at 110°, the following results :

LEGUMELIN.		
	66	67
Carbon .....	53.33	53.23
Hydrogen .....	6.87	6.88
Nitrogen .....	16.28	16.35
Sulphur .....	0.85	1.00
Oxygen .....	22.67	22.54
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.20	0.41

The filtrate from 67 was concentrated by dialysis in alcohol and the proteid so precipitated filtered out, washed with absolute alcohol, and redissolved in a little water. This solution was dialyzed and found wholly free from globulin, and also from coagulable proteid. The solution was then precipitated by pouring into much alcohol and the substance so separated dried and analyzed.

PROTEOSE, 68.	
Carbon .....	50.17
Hydrogen .....	6.77
Nitrogen .....	16.81
Sulphur .....	1.27
Oxygen .....	24.98
	<hr/>
	100.00
Ash .....	1.03

As already stated, the solution of the first ammonium sulphate precipitate of the proteids contained in the original extract was divided into two parts, which were dialyzed separately. The precipitate so produced in part II was dissolved in 500 cc. of two per cent. brine and 750 cc. of water added, giving an abundant precipitate, which was washed with water and alcohol and dried over sulphuric acid. This preparation, 69, wholly free from coagulable proteid, weighed nineteen grams and had, when dried at 110°, the following composition :

LEGUMIN, 69.

Carbon.....	51.91
Hydrogen .....	7.11
Nitrogen .....	17.91
Sulphur.....	0.38
Oxygen .....	22.69
	<hr/>
	100.00
Ash .....	0.62

In order to further fractionate preparations 59 and 69, quantities of each were mixed together, dissolved in five per cent. salt solution and filtered from a very small amount of insoluble matter. That any acid possibly present in combination with this globulin might be neutralized, three-tenths per cent. potash solution was cautiously added until the solution reacted just perceptibly alkaline with litmus paper. This solution was then dialyzed over night and the precipitate which separated was filtered out and the filtrate dialyzed twenty-four hours longer, giving a second precipitate, which was washed and dried as usual, forming preparation 70, while the first dialytic precipitate was redissolved in ten per cent. brine, filtered perfectly clear and again dialyzed over night. The precipitate which separated was prepared for analysis in the usual manner and formed preparation 71. These two products were found to be free from coagulable matter and to have the following composition, which is essentially the same as that of the preparations from which they originated:

LEGUMIN.

	70	71
Carbon .....	51.85	51.74
Hydrogen .....	6.88	6.87
Nitrogen .....	18.07	18.09
Sulphur .....	0.37	0.39
Oxygen.....	22.83	22.91
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.56	0.44

Since legumin has been described as soluble in water, 400 grams of lentil meal were twice treated with two liters of water, and strained on bolting-cloth. The extract was allowed to settle over night, and the somewhat turbid liquid (four liters) was siphoned off and saturated with ammonium sulphate. The precipitated proteids were treated with dilute brine, in which nearly



all dissolved. The solution was filtered clear and dialyzed for forty hours; the resulting precipitate, weighing, when dried, seven grams, was analyzed with the following results :

LEGUMIN, 72.

Carbon.....	51.65
Hydrogen.....	6.90
Nitrogen.....	18.05
Sulphur.....	0.38
Oxygen .....	23.02
	<hr/>
	100.00
Ash .....	0.64

One more extraction was made in the following manner: To 1200 grams of lentil meal, six liters of water were added which held in solution, 6.21 grams of baryta, the amount which had previously been determined to yield an extract neutral to litmus. After thoroughly mixing with the meal and breaking up all the lumps, six liters of ten per cent. salt solution were added. Unlike extracts not neutralized or neutralized with soda or potash, the insoluble matter in this case formed large flocculent masses which rapidly settled. The insoluble matter was strained out on bolting-cloth and the nearly clear extract was saturated with ammonium sulphate. The proteid thus separated was filtered out, dissolved in water, and dialyzed for three days. The greater part of the globulin was thus separated. It was filtered out and the filtrate was treated as described on page 372. The precipitate was dissolved in two per cent. brine and diluted until the solution contained 1.25 per cent. of salt. After depositing the resulting precipitate the solution was decanted and the precipitate was five successive times redissolved in fifty cc. of ten per cent. brine and thrown down by diluting to 400 cc. with water. The final precipitate, which was free from coagulable globulin, was washed with water and alcohol and dried. It weighed 15.85 grams and had the following composition :

LEGUMIN, 73.

Carbon .....	51.63
Hydrogen .....	6.95
Nitrogen .....	18.00
Sulphur.....	0.43
Oxygen .....	22.99
	<hr/>
	100.00
Ash .....	0.33

The solutions, resulting from the five just mentioned precipitations, and containing about one per cent. of salt, were diluted with an equal volume of water, forming a one-half per cent. salt solution. Proteid was thus precipitated which when dry weighed 20.25 grams, but was not further examined as it was doubtless a mixture of legumin and vicilin. The solution decanted from the foregoing precipitate was dialyzed for four days whereby 9.35 grams of preparation 74 were obtained having the following composition :

## VICILIN, 74.

Carbon .....	52.15
Hydrogen .....	6.81
Nitrogen .....	17.21
Sulphur.....	0.14
Oxygen .....	23.69
	<hr/>
	100.00
Ash .....	0.26

The filtrate described on page 371 from which the greater part of the globulin present in the extract had been separated by dialysis, was saturated with ammonium sulphate, the precipitate produced dissolved in a little water, and the solution filtered clear and dialyzed for seven days, when it was filtered from a small precipitate which analysis showed to be probably a mixture of vicilin and legumelin. The solution was returned to the dialyzer and the dialysis continued several days but nothing more separated. The solution was then concentrated by dialysis in alcohol and the precipitated proteid was dehydrated with absolute alcohol and dried. This preparation was then extracted with water, the residue remaining washed with alcohol, dried, and analyzed :

## LEGUMELIN, 75.

Carbon .....	53.10
Hydrogen .....	6.91
Nitrogen .....	16.16
Sulphur.....	1.09
Oxygen .....	22.74
	<hr/>
	100.00
Ash .....	0.56



	LEGUMELIN.					
	50	65	66	67	75	Average.
Carbon . . . .	53.31	53.02	53.33	53.23	53.10	53.20
Hydrogen . .	6.71	....	6.87	6.88	6.91	6.82
Nitrogen... .	16.08	16.36	16.28	16.35	16.16	16.25
Sulphur ...	0.97	...	0.85	1.00	1.09	0.98
Oxygen....	22.93	....	22.67	22.54	22.74	22.75
	-----	-----	-----	-----	-----	-----
	100.00	.....	100.00	100.00	100.00	100.00

PROTEOSE, 68.

Carbon .....	50.17
Hydrogen .....	6.77
Nitrogen .....	16.81
Sulphur.....	1.27
Oxygen .....	24.98
	-----
	100.00

The quantity of proteid extracted by water and precipitated by dialysis was determined for the lentil, as follows :

To 200 grams of fine ground meal one liter of water was added; the mixture was poured upon a sieve and the lumps broken up by washing them through with another liter of water. After mixing and standing a short time, the coarse residue was strained out on bolting-cloth, and the fine suspended matter allowed to settle over night at a low temperature. The solution was then siphoned off, filtered perfectly clear on a pulp filter, the first 300 cc. containing the water retained in the pulp being rejected, and one liter of the clear undiluted extract next passing the filter dialyzed as long as anything precipitated. In this way 9.76 per cent. of proteid was recovered, which contained 17.32 per cent. of nitrogen, showing the substance to be nearly pure globulin.

This operation was repeated with the same quantities and proportions of materials, but with the addition of just enough baryta to the water to give an extract perfectly neutral to litmus. On dialysis 13.72 per cent. of globulin was obtained, a considerably larger quantity than that yielded by the unneutralized extract. Although the globulins extracted from the lentil by brine are legumin and vicilin, identical in composition and properties with those from the pea, yet the proportion extracted by water from

the lentil is much greater, especially when the acid of the seed is neutralized to litmus.

A rigid comparison of the reactions given by the aqueous extracts of the lentil, both acid and neutral, showed no difference whatever, and in these reactions the extracts agreed strictly with those similarly obtained from the pea, except that with calcium chloride and sulphate heavy precipitates were obtained, readily soluble in a slight excess of calcium or sodium chloride. Extracts of the pea gave only slight precipitates with calcium chloride and none with calcium sulphate.

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## ON THE SPEED OF COAGULATION OF COLLOID SOLUTIONS.

BY C. E. LINEBARGER.

Received April 2, 1898.

ONE of the prettiest of projection experiments is the exhibition of the formation of crystals of salts, as ammonium chloride and oxalate, etc. The crystals seem fairly to shoot out over the screen. This speed of crystallization, so strikingly shown by the lantern, appears to be a characteristic property of solutions varying with the nature of the salt and solvent, the temperature, the degree of supersaturation, etc. So far as I know, no careful quantitative work has ever been done on the subject; some rough determinations that I have made with solutions of potassium nitrate indicate that the speed of crystallization is one or two millimeters per second.

Although there is a dearth of data on the subject, it will probably be conceded that the speed with which crystalloidal substances separate out of solution, is comparatively rapid; that is to say, the crystallizing solid traverses appreciable distances in a second or so.

Crystallization does not supervene unless the solution be supersaturated with respect to the solid, and there be at least a trace of a crystal already present to induce the crystallization; a supersaturated solution is then in an unstable condition.

Solutions of many colloids can be made to coagulate or gelatinize by the addition of a mere trace of certain substances. The striking analogy between this phenomenon and that of crystallization has often been mentioned and insisted

upon. Solutions of colloids behave as if they were supersaturated and required but a chance to pass over into the solid condition. We cannot expect the speed of coagulation to be very great, for we know how slow is the diffusion of colloids in solution. Still, if there is a true analogy between the processes of crystallization and coagulation, the addition of a small amount of a substance having the power to start coagulation in one part of a colloid solution should result in the spread of the coagulation at a certain rate throughout the whole solution, just as happens in the case of crystalloids in supersaturated solution.

The following experiments have been performed with the object in view of ascertaining whether the analogy presumed to exist in the behavior of solutions of colloids and of supersaturated solutions of crystalloids can stand the test of a severer scrutiny than has yet been accorded it.

#### PRELIMINARY EXPERIMENTS.

Two glass tubes of about five mm. bore were bent twice at right angles so as to form wide J-tubes; they had almost identical shapes. These tubes were held in a support side by side, and filled with a solution of colloidal iron prepared as follows:

To a very strong solution of pure ferric chloride in water, an almost saturated solution of ammonium carbonate was added in small portions with thorough agitation until the point of permanent precipitation was nearly reached. The resulting dark red solution was subjected to dialysis in parchment paper tubes until the outside water after twenty-four hours' contact with the tubes showed but faint traces of chlorine.

An analysis of the solution showed that it contained 20.563 grams iron and 7.128 grams chlorine to the liter; as is seen, a not inconsiderable amount of chlorine had refused to pass through the parchment paper.

A thin glass rod was dipped into dilute sulphuric acid, the drop clinging to it when removed was shaken off, and then the end on which but a faint trace of the acid remained was touched to the surface of the solution of iron; coagulation at once supervened at the surface. The tubes were then carefully stopped up with plugs of wax.

The accompanying table summarizes the observations of the

position of the coagulum after certain time-intervals and the speed of propagation of the coagulation ; this speed is the ratio of the distance in centimeters passed over by the coagulum to the time in seconds between two observations. No provision was made for keeping the temperature constant, which may have varied by as much as  $15^{\circ}$ – $20^{\circ}$ . The behavior of the solution in both tubes was very nearly the same, so that their mean is given.

SPEED OF PROPAGATION OF COAGULATION OF COLLOID IRON SOLUTIONS.

Time in seconds.	Distance in centimeters.	Speed.
$36 \times 10^3$	0.30	$833 \times 10^{-7}$
210	0.70	402
470	0.55	212
734	0.25	94
877	0.10	71
1308	0.35	80
*2641	*0.55	41
3505	0.15	17
4368	0.10	2
6096	0.11	5
14736	0.12	1
43656	0.20	0.8

The table shows that the speeds decrease continually until they practically vanish. The greater speeds at the beginning of the experiment are probably due to the diffusion of the sulphuric acid. It seems not at all unlikely that sulphuric acid enters into chemical combination with dissolved colloidal iron, forming an insoluble compound ; a comparatively small amount of the acid suffices to neutralize and precipitate a large quantity of iron oxide in the colloid state. Whitney's<sup>1</sup> experiments on certain compounds of chromium sulphate seem to be in accord with this view. If it be true, the precipitation of colloids from solution is not a physical phenomenon of supersaturation, but rather one of chemical combination.

It was thought that possibly the exceedingly small speed observed after the lapse of several days (marked with stars in the table) was not due to the spread of the coagulation but to mechanical jarring and gravity, for the coagulum was in the vertical portion of the tubes and the laboratory was subject to considerable jarring from the busy traffic of the street. The

<sup>1</sup> *Ztschr. phys. Chem.*, 20, 40, 1896.

appearance of the coagulum seemed to confirm this, for at the end of the time marked with a star in the table, it had lost the resemblance it at first had to a stack of inverted hollow cones fitting loosely into one another and had assumed the form of piles of disks like rouleaux of coins. In subsequent experiments only horizontally placed tubes were employed in a room quite free from mechanical vibrations.

#### DESCRIPTION OF APPARATUS.

A glass tube of about a millimeter bore and twenty cm. in length was fused in the side of a six-inch test-tube so as to be perpendicular to its axis; its extremity was drawn out in a long capillary and turned up through a right angle. A millimeter scale was attached to the horizontal arm.

The solution under investigation was poured into the tube thus prepared and then warmed up to about  $40^{\circ}$  so as to prevent the subsequent appearance of air-bubbles that might lodge in the narrow tube and separate the column of solution. The apparatus was then fixed in a stand and the end of the capillary tube sealed, and the substance intended to introduce coagulation introduced. A soft cork was inserted in the test-tube and pushed down somewhat; upon this a little mercury was poured and over the mercury a layer of melted wax. In this way evaporation of the solution was prevented. If a speed of coagulation ensued the coagulum would proceed in the horizontal tube where its progress could be measured.

#### EXPERIMENTS WITH COLLOID IRON SOLUTION.

The solution was prepared as described on page 376. Its analysis showed it to contain per liter 13.763 grams iron and 2.139 grams chlorine.

A tube was filled with this solution (A) and a second one with the solution diluted with twice its volume of water (B). Coagulation was started in both cases by the addition of a trace of sulphuric acid.

*Solution A.*—The coagulum at first nearly filled the test-tube but did not enter into the side tube; it gradually settled down so that now after twenty months it occupies the lower portion of the tube only below the mouth of the side tube. The solution



still has the characteristic red color of dissolved iron but not quite so dark as that of the stock solution. The sulphuric acid added seems to have been insufficient to enter into combination with all the iron.

*Solution B.*—The sulphuric acid added was sufficient to precipitate all the iron in the test-tube. The coagulum at first filled all the main tube and penetrated three millimeters into the side tube. As the coagulum settled, it left the supernatant liquid clear and colorless, while the filament of coagulated iron oxide advanced a little into the horizontal tube. In about six months the coagulum had settled below the side opening leaving a detached filament in the side tube. In the fourteen months, since, the filament has not advanced half a millimeter. Furthermore, while in the vertical tube the liquid is colorless, on the farther side of the plug of coagulated iron oxide, the solution still has a reddish color; the plug appears to act as a semipermeable membrane preventing the farther diffusion of the acid, if, indeed, all the acid has not already entered into combination.

#### EXPERIMENTS WITH COLLOID SILICIC ACID SOLUTIONS.

The solution of colloidal silicic acid was prepared by adding dilute hydrochloric acid to a solution of sodium silicate and dialyzing the resulting mixture until nearly free from chlorine. It was observed that if the dialysis was allowed to proceed until all chlorine detectable by silver nitrate solution had left the parchment paper tubes, the solutions generally coagulated as soon as poured into the test-tube or very soon afterwards. A small amount of chlorine, however, kept the solutions from coagulating for a long time. I have now a couple of solutions prepared as above over two years ago which apart from a very slight precipitate in the bottom of the bottles show no signs of coagulation; they are opalescent and contain a little chlorine.

An analysis of the solutions employed in ascertaining the presumed speed of coagulation resulted in 7.3276 grams silica and 0.0374 gram chlorine to the liter.

Two tubes similar to the one described on page 378 were filled with this solution and the following substances added to start coagulation: 1. Some of the solution was boiled and the crusts appearing around the edges of the dish as the water boiled away

were washed and added to the solution in the tube. 2. A portion of the silicic acid was coagulated with a little lime-water, the coagulum washed and added.

These tubes have been under observation for over twenty months and have not shown any tendency towards a spread of coagulation. Apart from an extremely slight precipitation they have the same appearance to-day as when first prepared.

#### EXPERIMENTS WITH SOLUTIONS OF EGG ALBUMEN.

The white of a fresh egg was cut through many times with a pair of scissors and mixed with three times its volume of water and filtered. A few drops of toluene were added to the filtrate and the whole thoroughly shaken together.

A tube was filled with this solution and some carefully washed coagulated albumen obtained by adding nitric acid to a portion of the same solution added.

The tube has been standing now for about twenty months, and no trace of a spread of coagulation is discernible. The coagulated albumen added has settled down to the bottom of the test-tube, and the solution has turned slightly yellow. There is no indication of putrefaction, however; the toluene seems to prevent that very well.

#### CONCLUSIONS.

The above experiments, made with solutions of colloids of quite different nature, seem to prove that coagulation started in one part of a solution does not necessarily spread through the whole body of the solution. The analogy assumed hitherto between colloid solutions and supersaturated crystalloid solutions does not seem to be more than seeming, and has no foundation in fact. It is extremely improbable that colloid solutions are comparable with supersaturated solutions.

CHICAGO, ILLINOIS, MARCH, 1898.

## NEW BOOKS.

**DAS OPTISCHE DREHUNGSVERMÖGEN ORGANISCHER SUBSTANZEN UND DESSEN PRAKTISCHE ANWENDUNG. BEARBEITET VON DR. H. LANDOLT, Professor der Chemie an der Universität zu Berlin. Unter Mitwirkung von DR. O. SCHÖNROCK, DR. P. LINDNER, DR. SCHÜTT, DR. L. BERNDT, DR. T. POSNER. Zweite gänzlich umgearbeitete Auflage. Mit Abbildungen. xxiv + 655 Seiten. Braunschweig: Vieweg und Sohn. 1898. Price, M. 18.**

The property of certain substances, of rotating the plane of polarized light, has long been known and has been the object of much research. The practical applications of this knowledge, however, attained a high degree of accuracy and usefulness before the theory of the phenomenon was understood or any but the most superficial explanations were offered for it. The way was first opened to definite knowledge concerning the cause of the rotatory powers of chemical compounds when, in 1874, J. H. van 't Hoff, of Utrecht, and J. A. LeBel, of Paris, announced in papers, separated by only a few weeks, a new theory; *viz.*, that optical activity stood in intimate relation to chemical structure. Indeed this was the beginning of a new epoch in chemical science. In sympathy with the suddenly developed interest in the subject, Professor Landolt, then of the Polytechnic School at Aix-la-Chapelle, brought out in 1879 a modest work of 237 pages, entitled "Das optische Drehungsvermögen organischer Substanzen und die praktische Anwendung Desselben." At that time this was the only work in existence which summed up what was known on the subject. In the nineteen succeeding years no other branch of chemistry has shown greater development or offered more complete and convincing verification of a fundamental theory than that called stereochemistry. Indeed such a mass of proof has been presented that the van 't Hoff-LeBel hypothesis has been generally accepted. In this new edition of his work the author says, "The principle of the asymmetric carbon atom may be designated as one of the best established theories of chemistry."

The second edition of Professor Landolt's monograph naturally records the immense strides made in this field. The book itself has grown to 655 pages and the number of optically active bodies known in 1879, *viz.*, 300, has increased to 700, for which

the specific rotation has been calculated with more or less attention to the conditions affecting accuracy. So far as the writer is informed this still remains the only work of its kind, but no number of rivals could diminish the appreciation one feels when he realizes the immense amount of material which has been carefully digested and notes the clear and systematic form of its presentation. Even the mechanical features of the book, the paper and the clear type of different sizes which the German book-makers so successfully employ to indicate the relative values of sections and paragraphs, are in keeping with the beautiful phenomenon, and the elegant theory to which it is devoted. It is written from the chemist's standpoint with such exposition of purely physical principles as to render them intelligible to other than physicists. No important details are omitted, but it is apparent that much of doubtful authenticity has been excluded. The literature citations are quite full, and this, of course, is of great value in a book of this kind. An interesting feature is the frequent and appropriate reference to the historical features of certain theories and reactions. The practical applications made of the rotatory powers of such substances as the carbohydrates, alkaloids, camphor, etc.; descriptions of the various instruments employed in the measurement of this power with directions for their use; all receive their full share of attention.

Those who have not followed recent advances in this field will find here admirable summaries of researches and important generalizations not otherwise accessible except as diffused through journals. It is of interest to learn that while in 1879 only four substances were known to exist in different optical modifications, *viz.*, tartaric acid, maleic acid, camphor, and camphoric acid, now over one hundred are recorded, of which most are known in the laevo, dextro, and inactive forms. Interesting sections are devoted to the formation and separation of racemic compounds, describing the methods used with such fruitful results by Fischer, Liebermann, Ladenburg, Lewkowitsch, Frankland, and others. Considerable space is devoted to the discussion and summing up of our knowledge of multirotation, the puzzling phenomenon concerning which many theories have been advanced and none accepted. Professor Landolt expresses himself to the effect that it is settled that the cause of multirota-

tion of sugars is to be found in the existence of isomeric modifications which in aqueous solutions are transformed (*umgewandelt*) the one into another.

The chief divisions of the work are six; *viz.*, I. General Discussion of Optical Activity; II. Physical Laws of Circular Polarization; III. Specific Rotation; IV. Apparatus and Methods for Determining Specific Rotation; V. Practical Applications; VI. Rotation Constants of Active Bodies.

The work is admirable from every standpoint and will be indispensable to the chemist or physicist who hopes to maintain footing in this important field.

W. E. STONE.

SPECTRUM ANALYSIS. BY JOHN LANDAUER, LL.D.; authorized English edition by J. BISHOP TINGLE, PH.D., F.C.S. New York: John Wiley & Sons. x + 239 pp. Price, \$3.00.

This is the translation of Dr. Landauer's article in Fehling-Hell's *Handwoerterbuch*, which has been republished as a separate book. Dr. Tingle recommends it as a text-book for American students of chemistry.

While commending the book to the attention of chemists already familiar with the principles of spectroscopy, the reviewer does not think it adapted to the use of beginners. No connected directions are given for the adjustment and use of the spectroscope and spectrometer; not even a diagram showing the use of the various parts; no suggestions for practice in the identification of lines or detection of elements. In fact, the attention of the writer is mainly directed to work that requires the most expensive apparatus and practiced manipulation. While use is made, from the outset, of such terms as "D line," "K line," etc., we must proceed to Chapter IX, before reaching a cursory account of Fraunhofer's notation. In the introductory discussion of the properties of light, no attempt is made to connect the refractive index with  $\lambda$ : consequently "dispersion" must be treated aphoristically. Total reflection is ignored: consequently the third tube of the spectroscope remains an enigma. By neglecting interference, diffraction is explained so obscurely, that the subsequent exposition of Prof. Rowland's work would be incomprehensible, without outside help. Practical applications of spectroscopy, that would interest the chemist, rather than the astronomer, fare badly. The two lines devoted to forensic ex-

amination and the four which mention the spectroscopic control of the Bessemer, could not have been found without the index.

All of this merely proves that a cyclopedia article cannot do duty as a text-book, and it is to be hoped that the first five chapters will be recast for subsequent editions. The latter part of the work shows admirable industry in the collation and recalculation of material, and good judgment in the elimination of superseded and unsatisfactory data. Exception might be taken to the omission of Michelson's work with the refractometer, of reference to hypotheses concerning fluorescence, and of discussions over atom-spectra and molecule-spectra. On the other hand, praise must be given to the lucid and impartial exposition of researches into the mathematical relations of spectral lines and their connection with chemical properties, as well as to the discussion of solar and astral spectra. It would be a valuable addition to the reference library of every chemist.

Dr. Tingle's translation is easy and idiomatic, the only solecisms being the persistent use of 'discovery,' for 'Erfindung,' and of the indefensible term 'magnetic current,' on page 75.

MORRIS LOEB.

ON LABORATORY ARTS. BY RICHARD THRELFALL, M.A., Professor of Physics in the University of Sydney. New York: The Macmillan Co. 1898. xii + 338 pp. Price, \$1.50.

The rather indefinite title of this book and the purpose for its existence, may be explained by quoting from the preface: "It is true that in a well-appointed laboratory, where apparatus is collected together in greater or less profusion, the appeal is often indirect, and to a student carrying out a set experiment with apparatus provided to his hand, the temptation to ignore the mechanical basis of his work is often irresistible. It often happens that young physicists are to be found whose mathematical attainments are adequate, whose observational powers are perfectly trained, and whose general capacity is unquestioned, but who are quite unable to design or construct the simplest apparatus with due regard to the facility with which it ought to be constructed. . . . It is the object of the following pages to assist the young physicist in making his first steps towards acquiring a working knowledge of 'laboratory arts.' "

The book is divided into four chapters, and the material con-

tained therein may be judged from the titles: Hints on the manipulation of glass and on glass-blowing for laboratory purposes, with an appendix on the preparation of vacuum tubes for the production of Professor Röntgen's radiation; glass-grinding and optician's work; miscellaneous processes; electroplating and allied arts, with an appendix on platinizing glass.

About one-third of the book is devoted to the many different manipulations of glass, as the use of blowpipes, glass-blowing, welding, grinding, fusing electrodes into glass, etc., in which the directions are, for the most part, clear and concise. Many of the methods offered differ from those already published, and with few exceptions only those methods are given which have met with success in the author's hands. This is more or less true of all processes given in the book. The appendix to Chapter I is a concise treatise on the preparation and the exhaustion of tubes for the production of Röntgen rays, the making of terminals and mercury pumps.

In the preface it is stated that "physical research is too difficult in itself, and students' time is too valuable, for it to be remunerative to work with insufficient appliances," but in spite of this, the greater part of Chapter II is devoted to lens-grinding, certainly a time-consuming operation, and which can hardly be classed as a laboratory art. In this chapter are also directions for making mirrors of glass and speculum metal.

Chapter III is devoted to such generally useful subjects as coating glass with aluminum and gold, cutting rock sections and sections of softer substances, soldering, etc. Thirty pages of this chapter are devoted to an excellent treatise on the preparation and properties of quartz fibers, and fifty pages to electric insulators and the properties and value of many substances used as insulators.

For the most part the directions throughout the book are well stated and to the point. An exception to this, however, is on the preparation of solutions for silvering mirrors (p. 151) in which the statement is awkward and unnecessarily involved. It is much to be regretted that a uniform system of measurement has not been adopted. Inches and millimeters, degrees Fahrenheit and Centigrade, are indiscriminately used. The index is well arranged and complete.

HENRY FAY.



**THE ARRANGEMENT OF ATOMS IN SPACE.** BY J. H. VAN 'T HOFF. Second revised and enlarged edition, with a preface by JOHANNES WISLICKNUS, and an appendix, Stereochemistry among Inorganic Substances, by ALFRED WERNER. Translated and edited by ARNOLD EILOART. London, New York and Bombay: Longmans, Green & Co. Cloth. xi + 211 pp. Price, \$1.75.

The writer recalls the amusement with which a modest brochure, entitled "*La chimie dans l'Espace*," was received in the leading laboratories of Europe, twenty years ago. Pleasantries, however, soon gave way to serious discussion, and that in turn was shortly followed by a widespread acceptance of the somewhat startling hypothesis of the young and comparatively unknown author, Professor J. H. van 't Hoff, of Amsterdam. Now he is recognized by all as the founder of what we term stereochemistry, and as having introduced into our science a concept as brilliant and daring as the theories which are associated with the names of Dumas, Laurent, Gerhardt, Kekulé, or Mendeléeff.

The present volume will be welcomed by the teaching profession as a standard text-book on stereochemistry. It presents all that is necessary for a student, in brief, compact form, and exhibits throughout the lucidity so characteristic of van 't Hoff's writings.

The historical portion is short and the question of priority with LeBel is handled in a courteous manner which does full justice to the talented French chemist. In the seven chapters devoted to carbon compounds, four are given to those containing one or more asymmetric carbon atoms, one to substances of the ethylene type, one to ring formation, and one to the important subject of the numerical value of the rotatory power. The presentation of theory and of experimental evidence is well balanced, while the lists of compounds involved are tabulated in a very clear and helpful manner. Points of existing controversy are fairly stated, and the author abstains from polemics. The fulness of bibliographic references and of the tabular statements is such, that the work rises notably above the level of a text-book and, despite its small size, can effectively replace Bischoff's large "*Handbuch der Stereochemie*." This result is attained in a great measure by a condensation of formulas. To a certain extent this practice is of doubtful advisa-



bility. The book will naturally be placed in the hands of comparatively young chemists. No device tending to bring out and emphasize the peculiar relations of the asymmetric carbon atom, should be neglected, at least in the early chapters. The use of a one-line formula, such as  $\text{CO}_2\text{HCHOHCH}_2\text{CO}_2\text{H}$ , while amply sufficient for the more advanced student, is to be deprecated at the beginning of the book. The additional space required for more ample graphic formulas, would be advantageously used from the standpoint of the teacher.

The chapter on the stereochemistry of nitrogen compounds is comparatively brief, as van 't Hoff's interest in this branch is less pronounced. The most recent results are, however, carefully summarized.

An appendix contains a note by Professor Werner on the stereochemical isomerism of inorganic compounds, confined, of course, to the amines of cobalt and platinum.

Dr. Eiloart has furnished an excellent translation and added in a few instances pertinent notes, introducing the results of recent investigations. It is a question whether the use of *right-handed* and *left-handed* for *dextro-rotatory*, etc., is to be recommended. A simpler expression for the Latin derivatives is undoubtedly desirable; but the introduction of the word *hand* recalls the Greek idiom, "bare-headed as to the feet," and certainly does not simplify the nomenclature.

Typographical errors are rare, but occasionally meet the eye, as in the formulas of malic and lactic acids, pages 29 and 163.

THOMAS H. NORTON.

BIBLIOGRAPHY OF THE PLATINUM GROUP, 1748-1896. BY JAMES LEWIS HOWE. Smithsonian Miscellaneous Collections, No. 1084. 8vo. pp. 318.

This forms a very valuable contribution to chemical bibliography, and will prove an indispensable aid to all workers in the field of the platinum metals. A glance at this volume is sufficient to show the great amount of labor expended upon it by Dr. Howe, and a closer examination will prove how faithfully and conscientiously the work has been done. Over one hundred sets of journals were consulted in its preparation, besides a large number of books, pamphlets, and single copies of periodicals. The total references number nearly 2500. They are first

arranged by years with the name of the author, followed by the title of the paper. Instead of a continuous consecutive numbering, however, the numbering is broken by each year and is consecutive for that year only. Nearly fifty pages are filled with a subject index in which the references are divided under sixty-six different headings. This makes the book particularly useful to a worker in any special field. An author index, filling some fifteen double-columned pages, completes the book.

Chemists owe a debt of gratitude to Dr. Howe for this tedious yet most helpful work, which he has so ably completed, and to the Smithsonian Institution for rendering its publication possible.

F. P. VENABLE.

**THE CALORIFIC POWER OF FUELS.** Founded on Scheurer-Kestner's *Pouvoir Calorifique des Combustibles*, with the addition of a very full collection of tables of heats of combustion of fuels, solid, liquid, and gaseous, to which is also appended the report of the committee on boiler tests of the American Society of Mechanical Engineers (December, 1897); table of constants used. By HERMAN POOLE, F.C.S. New York: John Wiley & Sons. 1898. xv + 255 pp. Price, \$3.00.

The general character of the book is pretty well indicated by the somewhat lengthy title. The first six chapters of the book are given, mainly, to a description of the various forms of calorimeters in common use for the determination of the heating power of fuels. The descriptions are satisfactory and include brief directions for the use of the more important forms of apparatus and an account of the corrections to be applied. Chapters VII to IX discuss solid, liquid and gaseous fuels chiefly from the standpoint of heating effect. Then follow three chapters devoted to the subject of boiler tests and the necessary determinations and calculations, especially those relating to loss of heat in waste gases. The Appendix includes the report of the committee on boiler tests referred to in the title, and very full tables, especially of the heating power of coals from all parts of the world. Unfortunately these tables, which the author appears to consider especially valuable, contain internal evidence that some of the values given are worthless. Thus, on page 216, three determinations for the same coal are given, with a difference of twenty-five per cent. between the highest and lowest values. Also, although most of the values are on the basis of

the coal burned to liquid water, in one case, at least, results which were published in terms of the fuel burned to vapor of water are given without the necessary correction. On page 106 analyses of natural gas are given which represent it as containing large amounts of hydrogen, although Professor Philips has, apparently, demonstrated<sup>1</sup> that this gas is never present. In the same table marsh gas and methane are given as though they were different substances. The value of the tables would be greatly increased if exact references to the source of the data were given.

While it is evident that the tables must be used with care and discrimination, the book will prove a useful one to engineers and chemists interested in the subject of fuels.

W. A. NOYES.

METHODS FOR THE ANALYSIS OF ORES, PIG IRON, AND STEEL. Easton, Pa.: The Chemical Publishing Co. 1898. 8vo. 131 pp. Price, \$1.00.

This well printed and neatly bound volume contains a symposium of methods of iron analysis, in use in the laboratories of iron and steel works in the region about Pittsburg, Pa., together with an appendix containing various special methods of analysis of ores and furnace products. The methods are given in detail by the chemists in charge of the fifteen laboratories represented and may be considered to represent the general practice of the chief iron and steel works in the principal center of the iron industry in the United States. When one reflects upon the vast commercial and manufacturing interests that are based upon the results of these methods of analysis, they become well worth careful study and comparison by every one interested in iron analysis.

P. W. SHIMER.

TEXT-BOOK OF PHYSICAL CHEMISTRY. By CLARENCE L. SPEYERS. iv + 224 pp. New York: D. Van Nostrand Co. Price, \$2.25.

There is a deplorable lack of continuity in the teaching of science between our universities and the schools preparing for them. While the student continues his study of languages and mathematics on entering college, he generally begins his study of science over again. Many students have had good courses in physics and chemistry in the secondary schools and are fitted to go on with that work in college. To such students as these,

<sup>1</sup> *Am. Chem. J.*, 16, 406.

as well as to those who may elect elementary courses in physical science during the first year or so of college, it seems highly desirable to offer a course in elementary physical chemistry. There is a vast body of knowledge lying between physics and chemistry which is of great interest and importance; it has in the main been obtained by what may be termed advanced methods, but its results can be advantageously presented in elementary form. A course presenting these results and the outlines of the methods employed in getting them seems a desideratum. Such a course would prove to be very profitable and beneficial; it would be an excellent "culture course" for those making physical science a minor subject, and a good preparatory course for those taking physics or chemistry as a major. It is a mistake to believe that the study of physical chemistry can be taken up with advantage only after a considerable acquaintanceship with the facts and theories of physics and chemistry has been made; the elements of these sciences are quite sufficient for a good comprehension of elementary physical chemistry. To insure the success of such a course, a text-book on physical chemistry corresponding in difficulty to our best elementary text-books on physics or chemistry is needed. The reviewer had hoped that the book at hand would fill this need, but finds it suited for quite advanced students only; and the need still exists.

This book represents what "the author" has been "in the habit of teaching the senior class in the chemical course in Rutgers College," and "is intended for self-instruction as well as classroom use." "The view that matter is a collection of energies in space" has been adopted; this view, due to a particular German school of physical chemists, gives the book throughout a peculiar complexion. Thus, on page 4 is found: "In ordinary chemical language we say chemical reaction takes place between definite weights of matter. In our language we should say the relation between the intensities of the distance energies (gravity energies) of two or more collections reacting to form another definite collection, is fixed." Another sample of the "energetic" style is this: "when the intensity of the heat energy is not relatively high, the intensity of volume energy is inversely proportional to the capacity only when the intensity of the volume energy is low," (p. 28) which probably means that

at low temperatures and high pressures gases do not obey Boyle's Law.

The author states (p. iv) : " With Ostwald, I feel convinced that the materialistic interpretation has passed its prime and has no promise for the future." This is an extreme and one-sided view. Careful study of Boltzmann's writings cannot fail to convince the fair and conscientious reader, no matter how biased he may be, that materialistic conceptions are necessary and useful ; and as for their help in discovering new truths, reference need only be made to the splendid confirmations by Zeemann, of Lorentz's atomistic views and theories.

The author goes further even than Ostwald in his classification of the kinds of energy. Chemical energy he rejects, because (p. 177) " the assumption of chemical energy is strictly gratuitous and not to be advised at all ;" but he makes up for this by adding internal energy, magnetic energy, and three kinds of radiant energy ; *viz.*, radiant heat energy, radiant light energy, and Roentgen ray energy. It seems rather strange that he has not added *mental* energy.

The book is something more than a text-book ; it is also an essay having for theme the dethronement of matter and the crowning of energy.

Some of the author's definitions are far from being clear and logical. For instance, " a chemical change is one in which the nature of the original body is very much changed," while " a physical change is a change which does not alter the characteristic chemical nature of the body." This amounts to saying : A change is a change or alteration ; a chemical change is a big change, while a physical change is a little alteration.

An original feature of the book is the introduction of numerous problems ; most of these are excellent and help greatly towards elucidating the text. A curious illustration of how facts may be made to fit theories is the following : The author in one of his problems (p. 81) assumes data given by the reviewer to be accurate enough to warrant the conclusion that " the benzene molecule seems to be polymerized nearly three times," while Bancroft (The Phase Rule, p. 118) thinks the same data to be at least ten per cent. in error. Both establish their theories, however.

The style of the book is concise and a mathematical treatment predominates. The historical development of any subject is avoided so that the reader hardly knows to whom he may attribute certain views advanced, by no means current among physical chemists. This avoidance of the historical treatment detracts much from the value of the book, for in such a subject where there still exists a conflict of views on many points, the only satisfactory treatment is the historical.

The statement of the author (p. iv) that "whoever works through" the book "conscientiously, paying particular attention to the problems, will get a very fair idea of physical chemistry," is, in the opinion of the reviewer, unwarranted. What the reader will get is a knowledge of a lot of subtle distinctions about energy, some practice in the handling of mathematical equations, and an incomplete acquaintance with some physico-chemical laws. But a "fair" idea of physical chemistry he certainly will not get.

C. E. LINEBARGER.

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### BOOKS RECEIVED.

**Spectrum Analysis.** By John Landauer, LL.D. Authorized English edition by J. Bishop Tingle, Ph.D., F.C.S. New York: John Wiley & Sons. 1898. x + 239 pp. Price \$3.00.

**The Sugar Beet in Illinois.** Bulletin No. 49. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 1898. 52 pp.

**The Cost of Production of Corn and Oats in Illinois in 1896.** Bulletin No. 50. University of Illinois, Agricultural Experiment Station, Urbana, Ill. 24 pp.

**An Ephemeris of Materia Medica, Pharmacy, Therapeutics and Collateral Information.** Vol. V, No. 1. January, 1898. By Edward R. Squibb, Edward H. Squibb, and Charles F. Squibb. Brooklyn, N. Y. 1898. 176 pp.

**Preparation and Application of Fungicides.** Bulletin No. 25. Connecticut Agricultural Experiment Station, New Haven, Conn. 1898. 16 pp.

**On the Crystalline Structure of Gold and Platinum Nuggets and Gold Nuggets.** By A. Liversidge, LL.D., F.R.S., Professor of Chemistry, University of Sydney, N. S. Wales. 10 pp. 16 plates.

**On Some New South Wales and Other Minerals. On the Amount of Gold and Silver in Sea-water. The Removal of Gold and Silver from Sea-water by Muntz Metal Sheathing.** By A. Liversidge, M.A., F.R.S., Professor of Chemistry, University of Sydney, N. S. Wales. 42 pp.

**Abbreviated Names for Certain Crystal Forms. Models to Show the Axes of Crystals.** By A. Liversidge, M.A., F.R.S., Professor of Chemistry, University of Sydney, N. S. Wales. 10 pp.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### PROTEIDS OF THE HORSE BEAN (*Vicia faba*).<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

THE only references which we have found to investigations of the proteids of this seed that at present have any importance are contained in papers by Ritthausen.<sup>2</sup>

In his earlier work<sup>3</sup> Ritthausen described as legumin the proteid extracted from the horse bean by potash water. Later<sup>4</sup>, he gave the results of treating the earlier preparations with salt solution and also of extracting the seeds with brine and precipitating the dissolved proteid by dilution or by acids, and concluded that the preparations which he obtained were mixtures of two proteids which could only be separated by dissolving in acid or alkali, precipitating by neutralization and extracting the precipitate with brine; the part dissolving he regarded as conglutin; that undissolved as legumin. A careful study of Ritthausen's work leaves us in much doubt respecting the nature of the proteids of this seed, and we have therefore undertaken the present investigation.

In order to avoid contaminating our preparations with tannin, which Ritthausen found to be present in considerable quan-

<sup>1</sup> Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

<sup>2</sup> Early references to legumin have been already noticed in our paper on "Legumin of the Pea and Vetch," Report of this Station for 1895, p. 262. This Journal, 18, 583.

<sup>3</sup> Die Eiweisskorper, etc., Bonn, 1872, p. 170.

<sup>4</sup> J. prakt. Chem., 26, 504, and 29, 448.

tity in the skin of these beans, we removed the greater part of the outer coating from the coarsely broken seeds by a current of air and the remainder by hand-picking. In this way it was possible to separate the brown outer seed-coat completely and by then grinding the broken beans to obtain a flour free from tannin.

A preliminary extraction made with this flour gave us a large yield of proteid which, in general, had nearly the properties and composition of the products similarly obtained from the pea and lentil, but differed throughout in containing less carbon than the corresponding substances from these other seeds, and in being, to a considerable extent, soluble in water. As these aqueous solutions reacted strongly acid with litmus and when neutralized gave precipitates soluble in brine which were reprecipitated by dilution, we were led to believe that the differences which we had found between the proteids of this seed and those of the pea, lentil, and vetch were due to a combination of the proteids with the acid of the seed. As this view appeared to be confirmed, we omit further details of our first extraction and proceed to an account of the second.

Two kilograms of the bean flour were treated with ten liters of ten per cent. salt solution, protected with thymol, and left over night in a cool place. The extract was strained through fine bolting-cloth and allowed to deposit suspended matter during two hours. The turbid liquid was siphoned off, centrifugated, and filtered nearly clear. The extract was then saturated with ammonium sulphate, the precipitate produced filtered out, removed from the paper, suspended in a little water and dialyzed for twenty-four hours, whereby so much of the sulphate was removed that the proteid dissolved. The solution so obtained was then filtered perfectly clear through a pulp filter and dialyzed for forty-four hours. The precipitate which had formed at first separated in spheroids, but these on settling united to a coherent mass, A, from which the solution B was decanted.

A portion of the precipitate A, weighing twenty-eight grams when air-dry, was washed thoroughly with water (in which it partly dissolved) and then with alcohol and dried at 110° for analysis.



LEGUMIN, 76.<sup>1</sup>

Carbon .....	51.55
Hydrogen .....	6.91
Nitrogen .....	18.12
Sulphur.....	0.48
Oxygen .....	22.94
	<hr/>
	100.00
Ash .....	0.54

The remainder of precipitate A was dissolved in brine and the resulting solution, having an acid reaction, was neutralized to litmus by adding very dilute potash water. This required 0.36 gram of potassium hydroxide. The slightly turbid solution was filtered absolutely clear and dialyzed for forty-eight hours. The large precipitate which resulted was found to dissolve completely in brine and to yield a perfectly neutral solution, which, when heated in a boiling water-bath, gave some coagulum. A portion of this precipitate was washed with water and alcohol, dried at 110°, and analyzed.

LEGUMIN, 77.

Carbon .....	51.87
Hydrogen .....	6.97
Nitrogen .....	18.05
Sulphur.....	0.38
Oxygen .....	22.73
	<hr/>
	100.00
Ash .....	0.84

The remainder of this substance was dissolved in 250 cc. of three per cent. brine and the solution diluted to 600 cc. A rapidly settling precipitate resulted which formed a fluid deposit from which the somewhat turbid mother-liquor was soon decanted; the proteid was washed thoroughly with water and alcohol, yielding when dry 19.13 grams of preparation 78.

LEGUMIN, 78.

Carbon .....	51.79
Hydrogen .....	7.06
Nitrogen .....	18.10
Sulphur.....	0.40
Oxygen .....	22.65
	<hr/>
	100.00
Ash .....	0.79

<sup>1</sup> Numbered consecutively with the preparations of the proteids of the lentil. This Journal, 20, 362.

The solution decanted from 78 was diluted with 150 cc. of water and a second precipitate obtained, wholly like the first, which when dried weighed eleven grams and had the following composition :

## LEGUMIN, 79.

Carbon .....	51.90
Hydrogen .....	6.94
Nitrogen .....	18.12
Sulphur.....	0.38
Oxygen .....	22.66
	<hr/>
	100.00
Ash .....	0.59

The solution from which 79 had separated was further diluted with 500 cc. of water and allowed to stand over night in a cool room. The next morning the solution was decanted from a small precipitate that had settled out. This, after drying, weighed five grams and had the following composition :

## LEGUMIN, 80.

Carbon .....	51.92
Hydrogen.....	7.04
Nitrogen .....	18.11
Sulphur.....	0.30
Oxygen .....	22.63
	<hr/>
	100.00
Ash .....	0.60

The solution decanted from 80 was dialyzed for four days but only a trace of proteid separated. Preparations 78, 79, and 80 contained no trace of coagulable proteid and may therefore be considered to be pure legumin. Since, however, 77, of which these were fractions, was shown by this treatment to contain only a very little coagulable matter, it too is essentially pure legumin as indicated by the analysis.

Solution B, described on page 394, was further dialyzed for twenty-four hours and the resulting precipitate C filtered out and the filtrate D treated as described on page 397.

The precipitate C was dissolved in ten per cent. brine, and the resulting solution diluted until it contained one per cent. of salt. The precipitate that formed was filtered out and the filtrate added to solution D. The precipitate was again dissolved in

salt solution, filtered clear, exactly neutralized with dilute pot-ash water, and dialyzed for forty-eight hours.

The globulin which had separated was filtered out. The filtrate contained a little more proteid, which yielded a coagulum on heating in a boiling water-bath.

The globulin was dissolved in 200 cc. of two per cent. brine, and the solution diluted with 200 cc. of water, which threw down a precipitate from which the solution E was decanted and treated as further described, while the precipitate was redissolved in salt solution, which was then dialyzed for twenty-four hours.

The precipitate which finally resulted, after washing and drying, weighed sixteen grams, and when dried at 110° had the following composition :

GLOBULIN, 81.

Carbon .....	51.89
Hydrogen .....	7.03
Nitrogen .....	17.67
Sulphur.....	0.34
Oxygen .....	23.07
	<hr/>
	100.00
Ash .....	0.76

The solution filtered from 81 contained but little proteid, which coagulated on heating to 99°.

Solution E, on diluting with an equal volume of water, gave a precipitate that, when washed and dried, weighed 4.74 grams, having the following composition :

GLOBULIN, 82.

Carbon .....	52.31
Hydrogen .....	7.04
Nitrogen .....	17.70
Sulphur.....	0.21
Oxygen .....	22.74
	<hr/>
	100.00
Ash .....	0.57

Solution D, noted on page 396, being inconveniently bulky, was saturated with ammonium sulphate, and the precipitate thus separated was dissolved in a little water; the solution was filtered clear, and dialyzed for five days. The deposited substance was

filtered out and the filtrate F treated as described later. The precipitate was dissolved in brine, the solution obtained was filtered clear and dialyzed for three days whereby all but a trace of the proteid was precipitated. This was filtered out, dissolved in 100 cc. of two per cent. salt solution and precipitated by adding fifty cc. of water. After the proteid, thus thrown down, had settled, the supernatant liquid was decanted and fifty cc. more water added, which caused a second precipitation. The solution from which this had separated was then dialyzed and the globulin contained in it precipitated. Thus three successive fractions were obtained which, when washed and dried, weighed respectively 5.65, 3.87, and 2.73 grams. When dried at 110° and analyzed these were found to have the following composition :

## VICILIN.

	83	84	85
Carbon.....	52.53	52.53	52.40
Hydrogen.....	6.93	6.98	7.09
Nitrogen.....	17.18	17.61	17.54
Sulphur .....	0.19	0.10	0.13
Oxygen.....	23.07	22.78	22.84
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Ash.....	0.26	0.18	0.13

Filtrate F, from which the substance yielding the three preceding preparations had been derived, was further dialyzed for seven days until freed from sulphates, which caused the separation of a small precipitate that, when filtered out, washed, and dried, weighed 1.64 grams and gave the following results on analysis :

## PROTEID, 86.

Carbon .....	52.43
Hydrogen .....	6.87
Nitrogen .....	16.42
Sulphur.....	} 24.28
Oxygen .....	
	<hr/>
	100.00
Ash .....	0.28

The filtrate from 86 was then heated to just 60° for about two hours, which caused a coagulum that was filtered out, washed

with hot water and with alcohol, dried, and found to weigh 1.60 grams. The filtrate from this coagulum was heated for some time at 75° and a second coagulum obtained, weighing 1.80 grams. Dried at 110°, the two preparations had the following composition :

LEGUMELIN.		
	87	88
Carbon .....	52.81	52.98
Hydrogen .....	6.98	6.89
Nitrogen .....	16.49	16.43
Sulphur.....	} 23.72	1.32
Oxygen .....		22.38
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.23	0.33

These two preparations are probably legumelin, although their carbon is distinctly less than that found in our preparations from other leguminous seeds. Since the solution from which these preparations separated had not been previously neutralized, we are inclined to ascribe this difference to an acid combined with the proteid.

The filtrate from 88 was next dialyzed against alcohol until all proteid matter was precipitated. This was filtered out, washed with absolute alcohol, dried, and found to weigh 6.78 grams. This preparation was dissolved in a little water, filtered from a slight insoluble residue; the solution was dialyzed for five days, then heated to boiling, and filtered from a trace of coagulum. The filtrate, which gave no precipitate on saturating with salt, was then concentrated to small volume over a water-bath and precipitated by pouring into alcohol. In this way 4.45 grams of proteose was obtained, which, when dried at 110° and analyzed, was found to have the following composition :

PROTEOSE, 89.	
Carbon .....	50.24
Hydrogen .....	6.66
Nitrogen .....	17.11
Sulphur.....	1.87
Oxygen .....	24.12
	<hr/>
	100.00
Ash .....	0.48

In order to confirm the foregoing results another extraction was made by treating 1200 grams of bean meal with 4200 cc. of water containing 9.44 grams of baryta, just enough to saturate the acid of the seed, using litmus as an indicator. This amount was ascertained by a careful preliminary test with 100 grams of the meal using a carefully standardized solution of baryta. After thoroughly mixing the meal with the water, an equal volume of ten per cent. brine was added, causing the gummy meal residue to separate in masses which settled quite rapidly and left the solution comparatively clear.

The residue was then strained out on fine bolting-cloth and the extract allowed to stand a short time, when it was siphoned from the sediment, filtered nearly clear, and saturated with ammonium sulphate. The precipitate produced was filtered out, suspended in water, and dialyzed over night. The next morning the solution of the proteid, which had resulted on dialyzing away the greater part of the adherent sulphate, was filtered and dialyzed for four days. A large precipitate of globulin separated which was filtered out and the filtrate G was treated as is subsequently described. The precipitate was redissolved in brine, filtered perfectly clear, and dialyzed for forty-two hours, whereby a large amount of globulin separated in form of spheroids that united on settling to a coherent mass. From this the solution H was decanted almost completely. The precipitate was dissolved in 500 cc. of two per cent. salt solution and the globulin again thrown down by diluting the salt solution to 1.33 per cent. After the large precipitate produced had settled, the solution I was decanted and the globulin redissolved in 100 cc. of ten per cent. brine and precipitated by diluting to 750 cc. As the substance still contained some coagulable matter it was redissolved four times in fifty cc. of ten per cent. brine and precipitated by diluting to 500 cc. The final precipitate gave only an opalescence on heating its solution in a boiling water-bath. Washed with water and with alcohol and dried over sulphuric acid, this preparation weighed forty-one grams, and had the following composition when dried at  $110^{\circ}$ :

LEGUMIN, 90.

Carbon .....	51.55
Hydrogen .....	7.03
Nitrogen .....	17.95
Sulphur.....	0.38
Oxygen .....	23.09
	<hr/>
	100.00
Ash .....	0.15

Solutions G, H, I, and those from the four last precipitations of 90 were separately dialyzed and the globulin which deposited was all dissolved together by adding fifty cc. of ten per cent. brine to water in which the substance was suspended. The resulting solution contained one and seven-tenths per cent. of salt and was diluted to a content of one and three-tenths per cent. This gave a precipitate on which the same treatment was repeated. The two solutions decanted from these precipitations were united and diluted with 200 cc. of water, the precipitate was united with the twice precipitated proteid just described and the solution J set aside for further treatment. The united precipitates were dissolved with fifty cc. of ten per cent. salt solution, and water added to 400 cc. The precipitate produced, which still yielded some opalescence in the boiling water-bath, was washed with water and alcohol, and, when dried, weighed 15.93 grams, and had the following composition :

LEGUMIN, 91.

Carbon .....	51.72
Hydrogen .....	6.95
Nitrogen .....	18.00
Sulphur.....	0.42
Oxygen .....	22.91
	<hr/>
	100.00
Ash .....	0.18

The solution decanted from 91 was united with solution J, before noticed, and diluted until the salt content was one per cent. After standing over night, the solution was decanted from the precipitate, which when washed and dried over sulphuric acid weighed nine and eight-tenths grams, and when dried at 110° had the following composition :

## LEGUMIN, 92.

Carbon .....	51.70
Hydrogen .....	7.12
Nitrogen .....	18.05
Sulphur.....	0.36
Oxygen .....	22.77
	<hr/>
	100.00
Ash .....	0.16

The solution decanted from 92 was dialyzed free from chlorides, the precipitate produced dissolved in one per cent. brine, and the solution diluted with an equal volume of water. After the proteid which separated had settled out, the solution was decanted and the deposit was washed with water and alcohol. When dry 14.41 grams of proteid were obtained, which were analyzed with the following results :

## GLOBULIN, 93.

Carbon .....	52.14
Hydrogen .....	7.08
Nitrogen .....	17.59
Sulphur.....	0.15
Oxygen .....	23.04
	<hr/>
	100.00
Ash .....	0.13

By adding a quantity of water to the solution decanted from 93 the globulin remaining in solution was precipitated and gave, when dried, 5.80 grams of proteid of the following composition :

## VICILIN, 94.

Carbon .....	52.36
Hydrogen .....	7.12
Nitrogen .....	17.43
Sulphur.....	0.10
Oxygen .....	22.99
	<hr/>
	100.00
Ash .....	0.10

Solution G, page 400, was saturated with ammonium sulphate, and the proteid thereby precipitated was dissolved in water, the solution filtered perfectly clear and dialyzed six days, when the precipitate produced was filtered out, washed, and treated as usual, giving preparation 95, weighing 4.23 grams.



PROTEID, 95.

Carbon .....	52.21
Hydrogen .....	7.12
Nitrogen .....	16.50
Sulphur.....	1.23
Oxygen .....	22.94
	<hr/>
	100.00
Ash .....	0.33

The filtrate from 95 was then heated to 65° in a water-bath, the coagulum filtered out, and the filtrate heated to 85°, which caused a second coagulum. The two preparations, 96 and 97, were washed with hot water, dehydrated with absolute alcohol, dried, and found to weigh 3.47 grams and 1.38 grams, respectively.

LEGUMELIN.

	96	97
Carbon .....	52.68	53.29
Hydrogen .....	7.14	7.05
Nitrogen .....	15.96	16.00
Sulphur.....	1.33	1.24
Oxygen.....	22.89	22.42
	<hr/>	<hr/>
	100.00	100.00
Ash .....	0.25	0.31

The filtrate from 97 gave no coagulum on boiling and was therefore saturated with salt, but as no precipitate formed, salt saturated acetic acid was added as long as proteid was thereby separated. The resulting precipitate was dissolved in water, filtered clear, and dialyzed till free from chlorides. The salt saturated filtrate was neutralized with sodium carbonate and also dialyzed till free from chlorides. Both solutions were next dialyzed in alcohol until concentrated to small volume, then were treated with excess of alcohol, and the precipitates obtained were filtered out. That from the salt saturated solution amounted to hardly more than a trace, while that from the acetic acid precipitate 98 weighed 4.14 grams.

PROTOPROTEOSE, 98.

Carbon .....	49.96
Hydrogen .....	6.76
Nitrogen .....	16.95
Sulphur.....	2.75
Oxygen .....	23.58
	<hr/>
	100.00
Ash .....	0.28

The large amount of sulphur found in this preparation was confirmed by a second closely agreeing determination. The small quantity of ash and the method of preparation make it impossible that this sulphur could be due to admixture of either calcium sulphate or ammonium sulphate.

In the horse bean, as in the pea and lentil, the proteids soluble in salt solution are legumin, vicilin, legumelin, and proteose. In the following tables the analyses of the purer preparations of these proteids may be readily compared :

LEGUMIN.									
	76	77	78	79	80	90	91	92	Aver.
Carbon .....	51.55	51.87	51.79	51.90	51.92	51.55	51.47	51.70	51.72
Hydrogen ..	6.91	6.97	7.06	6.94	7.04	7.03	7.02	7.12	7.01
Nitrogen ...	18.12	18.05	18.10	18.12	18.11	17.95	18.00	18.05	18.06
Sulphur ....	0.48	0.38	0.40	0.38	0.30	0.38	0.42	0.36	0.39
Oxygen .....	22.94	22.73	22.65	22.66	22.63	23.09	23.09	22.77	22.82
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

VICILIN.							
	82	83	84	85	93	94	Aver.
Carbon .....	52.31	52.53	52.53	52.40	52.14	52.36	52.38
Hydrogen ..	7.04	6.93	6.98	7.09	7.08	7.12	7.04
Nitrogen ...	17.70	17.28	17.61	17.54	17.59	17.43	17.52
Sulphur ...	0.21	0.19	0.10	0.13	0.15	0.13	0.15
Oxygen ....	22.74	23.07	22.78	22.84	23.04	22.99	22.91
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

LEGUMELIN.					
	87	88	96	97	Aver.
Carbon .....	52.81	52.98	52.68	53.29	52.94
Hydrogen .....	6.98	6.98	7.14	7.05	7.02
Nitrogen .....	16.49	16.43	15.96	16.00	16.22
Sulphur .....	23.72	1.32	1.33	1.24	1.30
Oxygen .....		22.38	22.89	22.42	22.52
	100.00	100.00	100.00	100.00	100.00

PROTEOSE.		
	89	98
Carbon .....	50.24	49.95
Hydrogen .....	6.66	6.76
Nitrogen .....	17.11	16.95
Sulphur .....	1.87	2.75
Oxygen .....	24.12	23.58
	100.00	100.00

In order to determine the amount of the proteids of this seed extracted by water, 200 grams of the fine meal were thoroughly mixed with 2000 cc. of water so that all lumps were broken up, and the coarse residue was strained out on bolting-cloth. After standing two hours, the greater part of the starch, etc., settled, and 1400 cc. of extract were siphoned off and filtered perfectly clear on a pulp filter, the first 300 cc. being rejected and the next 1000 cc. collected separately. The latter was dialyzed for four days, in which time all the proteid separable in this way deposited as spheroids. The precipitate, washed and dried, was equal to sixteen per cent. of the meal.

The process just described was exactly repeated save that enough baryta was at first added to make the extract neutral to litmus: the yield of proteid was eighteen per cent.

The proteid from the first extraction contained 1.16 per cent. of ash and, reckoned ash-free, 17.50 per cent. of nitrogen, showing it to be nearly pure globulin, while that from the second, neutralized extract, was less pure, as it contained 5.41 per cent. of ash and contained, ash-free, 16.96 per cent. of nitrogen. The reactions of these extracts were compared under identical conditions with the following result:

Both extracts, like those from the pea, lentil, and vetch, when poured into water gave, where the two fluids came in contact, a slight cloud which disappeared on shaking. Unlike the neutralized extract, as well as unlike both neutral and acid extracts of the other legumes, the unneutralized extract of the horse bean gave a heavy precipitate with sodium chloride, even with perfectly pure salt which we prepared from *pure* soda and *pure* hydrochloric acid and proved to be absolutely neutral. This precipitation of the globulin would indicate the presence of an acid compound, but the extract gave but a very slight precipitate on neutralizing with baryta, probably due to phosphates. The addition of acetic acid gave a large precipitate soluble in dilute brine, as did calcium chloride and calcium sulphate.

# PROTEIDS OF THE VETCH.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

IN order to further fractionate vetch globulin, we treated a quantity of preparation 17<sup>2</sup> with 900 cc. of three per cent. brine and, after filtering out the insoluble residue, we added an equal volume of water to the clear filtrate, and then cooled the mixture to 5°. The precipitate thus caused was washed and dried, forming preparation 99,<sup>3</sup> and the filtrate was diluted with an equal volume of water, which caused a second precipitate, preparation 100. The residue, insoluble in the three per cent. brine, had become swollen and gelatinous, as has always been observed with the insoluble form of legumin, so that it stopped the pores of the filter. It was therefore washed by decantation with salt solution and finally with water. As the salt was washed out the substance lost its gelatinous properties and became granular and easily filtered. It was next treated with one per cent. sodium carbonate solution, and the small portion insoluble therein was filtered out. The solution was partly neutralized with hydrochloric acid, and carbonic acid gas passed through it, which precipitated nearly all the dissolved proteid. This was filtered out, dissolved in brine, and the clear solution dialyzed. The substance thus separated, when washed and dried, formed preparation 101.

These three preparations were carefully analyzed with the following results :

LEGUMIN.			
	99	100	101
Carbon .....	51.72	51.52	51.79
Hydrogen .....	6.97	6.95	7.03
Nitrogen.....	18.13	18.08	18.03
Sulphur .....	0.43	23.47	23.15
Oxygen.....	22.75		
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

<sup>1</sup> Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.

<sup>2</sup> Annual Report of the Connecticut Agricultural Experiment Station for 1895, p. 277. This Journal, 18, 598.

<sup>3</sup> Numbered consecutively with the preparations of the proteids of the horse bean.

Another extraction was made by treating 500 grams of vetch meal with water and then with ten per cent. sodium chloride solution. After filtering clear, the salt extract was saturated with ammonium sulphate, the precipitate produced was dissolved in brine, the solution filtered perfectly clear, and dialyzed. In this way thirty-five grams or seven per cent. of the meal was obtained as preparation 102, having the following composition :

LEGUMIN, 102.

Carbon .....	51.62
Hydrogen .....	6.92
Nitrogen .....	17.88
Sulphur.....	0.50
Oxygen .....	23.08
	<hr/>
	100.00
Ash .....	0.23

Again, a quantity of vetch meal was digested in saturated salt solution and the dissolved legumin precipitated by dialysis. After drying at 110° this gave the following figures :

LEGUMIN, 103.

Carbon .....	51.86
Hydrogen .....	6.99
Nitrogen .....	17.97
Sulphur.....	} 23.18
Oxygen .....	
	<hr/>
	100.00
Ash .....	0.57

Another extraction was made by treating 1200 grams of meal with three liters of water containing enough baryta to exactly neutralize the acid of the seed when tested with litmus paper. After thoroughly mixing, three liters of ten per cent. salt solution were added and the residual meal strained out on fine bolting-cloth. After standing a short time the greater part of the starch settled and the liquid was siphoned off, filtered perfectly clear, and saturated with ammonium sulphate. The precipitate produced was filtered out, suspended in water, and dialyzed over night, whereupon the proteid dissolved. Its solution was filtered clear and dialyzed for two days with separation of a large precipitate.

This was filtered out and the filtrate A examined as will be described later. The precipitate was dissolved in brine, the solution filtered perfectly clear from a small amount of insoluble matter, and dialyzed for two days. The large coherent deposit was washed with water and with alcohol, and dried over sulphuric acid. This preparation, 104, weighed seventy-five grams and, as it was obtained from nearly three-fourths of the total extract, represented about ten per cent. of the meal. When dried at  $110^{\circ}$  and analyzed, the following results were obtained :

## LEGUMIN, 104.

Carbon .....	51.59
Hydrogen .....	7.07
Nitrogen .....	18.03
Sulphur.....	0.36
Oxygen .....	22.95
	<hr/>
	100.00
Ash .....	0.15

The filtrate A was returned to the dialyzer and, after three days, filtered from a small precipitate which, washed and dried, weighed six and a half grams and gave preparation 105, having the following composition :

## PROTEID, 105.

Carbon .....	51.81
Hydrogen .....	7.10
Nitrogen .....	17.07
Sulphur.....	0.57
Oxygen .....	23.45
	<hr/>
	100.00
Ash .....	0.38

The filtrate from 105 was saturated with ammonium sulphate and the precipitate produced filtered out, dissolved in as small a quantity of water as possible, the solution filtered clear, and dialyzed for seven days, when it was filtered from a small precipitate that was partly soluble in salt solution. This was washed with water and alcohol and formed preparation 106.

The filtrate from 106 was heated to  $65^{\circ}$  in a large water-bath and a coagulum obtained which, when filtered out, washed, and dried, formed preparation 107, weighing three and two-tenths grams. The filtrate from this, on heating to  $85^{\circ}$ , gave a small

coagulum that, when washed and dried, weighed only 0.88 gram, 108.

LEGUMELIN.

	106	107	108
Carbon .....	53.05	53.33	....
Hydrogen .....	7.29	6.93	....
Nitrogen.....	16.25	16.10	16.16
Sulphur .....	1.19	0.85	....
Oxygen.....	22.22	22.79	....
	<hr/>	<hr/>	<hr/>
	100.00	100.00	....
Ash .....	0.39	0.26	0.38

The filtrate from 108 gave no coagulum on boiling. It was concentrated, partially by evaporation and further by dialysis in alcohol. A small precipitate thus separated, which was dehydrated with absolute alcohol and dried, giving one gram of preparation 109, that contained 12.74 per cent. of ash and, reckoned ash-free, 15.71 per cent. of nitrogen.

The results show that the salt extracts of the vetch seed contain no other proteids than legumin, legumelin, and a very small proportion of proteose. Vicilin, which was found in the pea, horse bean, and lentil, is not present in detectable quantity in the vetch.

Our new analyses of these proteids are tabulated as follows :

LEGUMIN.

	99	100	101	102	103	104	Former Aver.	Former Aver.
Carbon.....	51.72	51.52	51.79	51.62	51.86	51.59	51.69	52.09
Hydrogen ...	6.97	6.95	7.03	6.92	6.99	7.07	6.99	6.88
Nitrogen ....	18.13	18.08	18.03	17.88	17.97	18.03	18.02	18.02
Sulphur.....	0.43	23.45	23.15	0.50	23.18	0.36	0.43	0.46
Oxygen.....	22.75			23.08		22.95	22.87	22.55
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

LEGUMELIN.

	20	106	107	108	Aver.
Carbon .....	53.55	53.05	53.33	....	53.31
Hydrogen .....	6.70	7.29	6.93	....	6.97
Nitrogen .....	16.46	16.25	16.10	16.16	16.24
Sulphur .....	1.02	1.19	....	....	1.11
Oxygen.....	22.27	22.22	....	....	22.37
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	....	....	100.00

## PROTEOSE, 22.

Carbon .....	50.85
Hydrogen .....	6.75
Nitrogen .....	16.65
Sulphur.....	} 25.75
Oxygen .....	
	<hr/> 100.00

## THE PROTEIDS OF THE PEA, LENTIL, HORSE BEAN, AND VETCH.<sup>1</sup>

BY THOMAS B. OSBORNE AND GEORGE F. CAMPBELL.

Received March 29, 1898.

As shown in our papers on the proteids of the pea, lentil, horse bean, and vetch, these seeds contain legumin, legumelin, and proteose, and the three first-named also contain vicilin. A careful comparison of the reactions and properties of these proteids, as now obtained by us, reveals no difference between preparations of the same substance from different seeds.

## LEGUMIN.

Legumin forms the chief proteid constituent obtainable from the vetch, pea, lentil, and horse bean. In the first-named seed about ten per cent. of the meal was found to consist of legumin; in the three other seeds this proteid is associated with vicilin, from which we have no method for its quantitative separation. From the pea about ten per cent., from the lentil thirteen per cent., and from the horse bean about seventeen per cent. of these mixed proteids were obtained. The lentil contains the least proportion of legumin, which seems to form about two-thirds of the mixed proteids, while the horse bean contains the greatest, as in this seed vicilin is present in relatively small amount.

Legumin is a globulin, for it dissolves readily in saline solutions and is precipitated therefrom either by dialysis, dilution, or cooling. By dialysis or by cooling it separates in the form of spheroids which, after settling from the solution, unite to form a plastic mass. By diluting its concentrated solutions the legumin separates as a viscid, translucent fluid. This fluid, when

<sup>1</sup> Reprinted from advance sheets of the Report of the Connecticut Agricultural Experiment Station for 1897. Communicated by the authors.



treated with water, becomes opaque and solid, so that the legumin can be converted into a coarse meal by rubbing with a glass rod under water. Conglutin from lupin seeds and amandin from almonds behave similarly, as do gliadin of wheat and rye and hordein of barley, when precipitated from alcoholic solutions by dilution with water.

Solutions containing more than two per cent. of sodium chloride dissolve legumin abundantly; those containing less salt have a solvent power rapidly decreasing with the diminishing salt content so that a one per cent. salt solution dissolves very little. Saturation with sodium chloride or magnesium sulphate does not precipitate legumin from its solution in brine, but saturation with sodium sulphate at 34° precipitates it almost completely.

In pure water legumin is entirely insoluble, but if the solution from which the legumin is precipitated contains acid, this may combine with the legumin and the resulting preparation, like other acid globulins, will then dissolve in pure water.

If seeds containing legumin are extracted with water, more or less of the legumin is dissolved; from the pea about four per cent., from the vetch two and a half per cent., from the lentil ten per cent., and from the horse bean sixteen per cent. The legumin thus dissolved is largely precipitated by dialysis in water, by the addition of acids and by lime salts and very slightly by great dilution with water. These aqueous extracts react strongly acid with litmus, and alkaline with lacmoid, a behavior doubtless due to acid potassium phosphates together with organic acids or acid salts, for acids combined with proteids do not react with lacmoid, although they readily turn blue litmus red. Solutions which we have made, of legumin from various seeds as well as of edestin from hemp-seed, by dissolving the proteid in monohydrogen potassium phosphate, have shown us all the reactions of these aqueous extracts excepting one presented by the horse bean, the unneutralized water extracts of which are precipitated with *pure* sodium chloride. This reaction we cannot explain, for these extracts give with dilute acids precipitates soluble in salt solutions and no precipitates on neutralization, reactions which seem to exclude the presence of acid globulin.

Solutions of legumin or of edestin in monohydrogen potassium phosphate behave more like solutions in dilute alkali carbonates than like solutions in neutral salts, for they give precipitates with dilute acids which are soluble in more acid or in salt solutions and are not precipitated by dilution unless very little phosphate is present. If phosphoric acid is added to the potassium phosphate solution, the solvent power of the phosphate is diminished and the facility with which the proteid is precipitated by dilution is increased; but if only little acid is added, yet enough to give a decided reaction with litmus, considerable quantities of the globulins are still dissolved and the reactions of solutions so made closely resemble those of the aqueous extracts of these seeds. As a result of numerous comparisons of the reactions of solutions so prepared with those of the aqueous extracts of leguminous seeds, we believe that the extraction of legumin by water from these seeds is due to the presence of acid potassium salts of phosphoric and organic acids, and that in consequence of the varying proportions of these substances in the different kinds of seeds, different amounts of legumin are thus extracted from them. As the proportion of phosphoric acid to potash in these leguminous seeds is much smaller than in most of the other seeds which we have examined, the character of the salts present may fairly be supposed to differ, and consequently the solubility of the proteids would also differ when the seeds are extracted with water. Thus in lupin seeds the amount of phosphoric acid, one and four-tenths per cent., exceeds that of the potash, one and one-tenth per cent., and from them water extracts but little proteid. Liebig and Ritthausen attributed the solubility of legumin to *basic* phosphates, and the latter undertook extensive experiments to show the presence of an excess of potash in the aqueous extracts, but such a supposition appears to overlook the fact that the aqueous extracts of these seeds are decidedly acid towards litmus.

Dissolved in dilute sodium chloride solution, legumin is precipitated by a little acetic acid, the precipitate being soluble in an excess of sodium chloride. The solubility of precipitates so produced depends on the relative proportions of salt and acid.

Legumin extracted without neutralizing the natural acid of the seed and precipitated by dialysis, either directly or after pre-

precipitation with ammonium sulphate, is usually converted to a large extent into insoluble "albuminate."

This "albuminate" differs from the similar insoluble products obtained from most other globulins, for when treated with salt solution it becomes gelatinous, cannot be filtered, and, on washing with water, shrinks, becomes opaque, and finally granular, so that it can be very readily washed on a filter. This substance appears to become hydrated by salt solution and dehydrated by pure water.

If the acid of the seed is previously neutralized, the globulin extracted by salt solution yields very little if any insoluble "albuminate," which indicates that the latter is a product of the action of the acid of the seed. This fact is in harmony with experiments described in a former paper of ours on the action of minute quantities of acid on globulins.<sup>1</sup> In very dilute acids and alkalies in absence of salts, legumin dissolves readily and abundantly, from which solutions, if at once neutralized, it is precipitated in a form soluble in sodium chloride solution. By this treatment no evidence of change has been detected. Solutions made with hydrochloric acid are precipitated by a small excess of acid, but those made with acetic acid are not precipitated by any excess of acid.

Solutions of legumin in ten per cent. sodium chloride brine are not rendered turbid by long heating in a boiling water-bath.

Dissolved in ten per cent. sodium chloride brine, legumin is precipitated by a very little hydrochloric acid, but a relatively considerable amount of acetic acid is required to produce a precipitate in such solutions.

Sodium chloride solutions of legumin give large precipitates with tannic acid as well as with picric acid, those formed by the latter dissolving in an excess of salt solution if too much picric acid had not been previously added. With mercuric chloride no precipitate is produced.

With nitric acid, Millon's and Adamkiewicz's tests, proteid reactions are obtained. With the biuret test a violet color is given which on standing becomes a deep rose-red like that given by peptones.

<sup>1</sup> Report of the Connecticut Agricultural Experiment Station for 1896, p. 369. This Journal, 19, 482.

Legumin has been supposed by some investigators to contain phosphorus and therefore to belong with the nucleo-proteids. A careful testing of thoroughly purified samples, by fusing with caustic soda and nitrate, and treating the solution of the fusion acidified with nitric acid with ammonium molybdate, showed that in some of the preparations only just detectable traces of phosphorus were present, while other preparations contained none whatever.

Although we have examined large numbers of our preparations of the different plant proteids for phosphorus, we have as yet found none which, in carefully purified samples, contained more than a few hundredths of a per cent., a quantity so small that it is reasonable to consider it as a constituent of the ever-present ash.

The composition of legumin is shown by the following figures, which are averages of a number of preparations from each of the different seeds :

	LEGUMIN.				
	Pea.	Lentil.	Horse bean.	Vetch.	Average.
Carbon .....	51.74	51.73	51.72	51.69	51.72
Hydrogen .....	6.90	6.89	7.01	6.99	6.95
Nitrogen .....	18.04	18.06	18.06	18.02	18.04
Sulphur .....	0.42	0.40	0.39	0.43	0.41
Oxygen .....	22.90	22.92	22.82	22.87	22.88
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

VICILIN.

Vicilin is a globulin associated with legumin in the pea, lentil, and horse bean. But as we have no means of separating vicilin and legumin quantitatively, we can state nothing respecting the amount in which it occurs in these seeds further than that the lentil contains the most and the horse bean the least. In the lentil it probably forms about one-third of the mixed globulins. That vicilin is not a derivative of legumin, is almost conclusively proved by the fact that no vicilin can be obtained from the vetch.

The most remarkable characteristic of vicilin is its content of sulphur, less than that of any other known proteid. This element, it may be noticed, diminishes in quantity with repeated

precipitation as though by this process sulphur were split off from the molecule. The total quantity, however, is so small that it might appear unsafe to draw conclusions from the differences observed, that is from 0.23 per cent. maximum to 0.08 per cent. minimum. Yet repeated determinations of this element have shown us that the differences were not analytical. It would seem possible by sufficiently repeated precipitation to obtain from this proteid preparations free from sulphur.

In salt solution vicilin is much more soluble than legumin, so that by repeated precipitation from diluted solutions the two globulins can be separated.

When solutions of vicilin in ten per cent. brine are heated in a water-bath they become turbid at 90° and at 95° flocks separate. When heated for some time at 100° this globulin is almost completely coagulated. In water, vicilin is insoluble. In one per cent. sodium chloride solution it dissolves considerably, while in slightly stronger solutions it is much more soluble, the solution of the globulin appearing to depend on the presence of enough salt to form a soluble compound.

In its other reactions it very closely resembles legumin.

The composition of vicilin we found to be as follows :

VICILIN.				
	Pea.	Lentil.	Horse bean.	Average.
Carbon.....	52.36	52.13	52.38	52.29
Hydrogen.....	7.03	7.02	7.04	7.03
Nitrogen .....	17.40	17.38	17.52	17.43
Sulphur.....	0.18	0.17	0.15	0.17
Oxygen .....	23.03	23.30	22.91	23.08
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00

#### LEGUMELIN.

We have found legumelin in all the leguminous seeds which we have examined with the exception of the white bean (*Phaseolus vulgaris*) and the blue and yellow lupin.

It is difficult to decide whether this proteid should be considered an albumin or a globulin.

By prolonged dialysis of solutions containing considerable legumelin a very small part separates, usually in a form insoluble in salt solutions. In one case we obtained a precipitate by

dialysis which was wholly soluble in brine, to a solution from which a relatively large coagulum separated on heating to 65°, thus indicating a globulin. We have found, however, that other proteids, notably edestin, undergo a change in solubility, whereby the proteid becomes gradually more and more difficult to dissolve. Thus edestin changes from a form insoluble in cold brine to one soluble in hot brine, also from one soluble in hot brine to one insoluble therein, but soluble in dilute sodium carbonate solution, and finally from a form insoluble in alkali carbonate to one soluble only in caustic alkali. It is not unreasonable to expect that a proteid which might properly be considered an albumin (*i. e.*, soluble in pure water and coagulable on heating) should undergo a similar change whereby it becomes no longer soluble in pure water but dissolves in salt solutions and then further changes to a form no longer soluble in brine but dissolved by alkali carbonates.

Such a very large proportion of the legumelin resists precipitation by dialysis, that we are inclined to regard the small precipitates which we have obtained in this way as due to changes similar to those which produce so-called "albuminates" from globulins.

In a paper on the proteids of the cow pea we designated this proteid as a globulin, but in view of our subsequent, much more extensive experience we now consider legumelin to be more properly classed with the albumins.

The amount of legumelin which we have found in the seeds discussed in this paper, was in the pea two per cent., vetch one and one-half per cent., lentil and horse bean one and one-quarter per cent.

No definite coagulation point can be stated for legumelin, as the presence of salts or acids as well as the proportion of dissolved legumelin have a great effect on the temperature at which coagulation takes place. Coagulated legumelin is soluble in very dilute alkalies, as is shown by the following experiment tried with preparation 41 from the pea. About seven-tenths gram of this substance which had been nearly dried over sulphuric acid, but which still contained some alcohol, was suspended in fifty cc. of water and ten cc. of one-half per cent. caustic soda solution added. The legumelin dissolved at once.

giving a glairy solution very similar in appearance to undiluted white of egg. After standing a few moments the viscosity disappeared and the solution became thin and clear. This solution was then almost neutralized by adding a nearly sufficient quantity of a dilute acetic acid which had been previously titrated against the soda solution. The liquid still remained clear and the legumelin was not precipitated until but a trace of the alkali remained unneutralized.

In dilute hydrochloric or acetic acid the coagulum is not soluble. By adding ten per cent. of sodium chloride to solutions containing legumelin, and then acetic acid, the acid compound of this proteid is precipitated, which dissolves in water to a solution that on neutralization gives a precipitate insoluble in water.

By saturating seed extracts, freed as far as possible from all globulin, with sodium chloride or magnesium sulphate only a very slight precipitate is obtained, showing that legumelin is thus slightly if at all precipitated.

Owing to the impossibility of separating legumelin from associated proteose, except in a coagulated state, we have learned but little respecting its reactions.

In the following table we give the average of analyses which we have made of coagulated legumelin from different seeds. These preparations have been obtained in a variety of ways, as can be seen by consulting our papers on the seeds named.

#### LEGUMELIN.

Source	Moisture	Protein	Carb.	Fat	Phosph.	Calc.
Pea	10.5	78.5	1.5	0.5	0.5	0.5
Lentil	10.5	78.5	1.5	0.5	0.5	0.5
Horse Bean	10.5	78.5	1.5	0.5	0.5	0.5
Vetch	10.5	78.5	1.5	0.5	0.5	0.5

## PROTEOSE.

As the proteose of these seeds is present in small amount and is difficult to obtain pure, we have not as much information respecting it as is desirable. The pea appears to contain about one per cent., the horse bean about one-half per cent., and the lentil and vetch evidently less. It is probable that more or less of this proteose may be lost by diffusion, for 10.5 grams of what was doubtless nearly pure proteose from the pea, after solution and dialysis yielded only about six grams when reprecipitated. We have obtained a few of the reactions of proteose from the pea and horse bean, but no reactions of this proteid from the lentil and vetch.

By saturation with salt, solutions of the proteose of the pea and horse bean are not precipitated, but by subsequently adding salt saturated acetic acid, a large part of the pea proteose separates while all but a trace of that from the horse bean is thrown down. Nitric acid in the aqueous solutions of the pea proteose gives no precipitate unless the solution is previously saturated with salt, when a precipitate, soluble on warming and reappearing on cooling, is given by that part of the proteose precipitable by acetic acid from a salt saturated solution, while the part not thus precipitable gives only a turbidity. Both these parts of the pea proteose are precipitated by copper sulphate, and give a rose-red biuret reaction.

The composition of the preparations from these seeds was found as follows :

	Pea.		Lentil.	Horse bean.		Vetch.
	46	47		89	98	
Carbon .....	50.24	49.66	50.17	50.24	49.96	50.85
Hydrogen .....	6.76	6.78	6.77	6.66	6.76	6.75
Nitrogen .....	17.35	16.57	16.81	17.11	16.95	16.65
Sulphur .....	1.25	1.40	1.27	1.87	2.75	25.75
Oxygen .....	24.40	25.59	23.98	24.12	23.58	
	100.00	100.00	100.00	100.00	100.00	100.00

46, Precipitated by saturating with salt and adding acetic acid.

47, From the filtrate from 46.



68, Total proteose precipitated by alcohol.

89, Ditto.

98, Precipitated from salt saturated solution by acetic acid.

22, Total proteose precipitated by alcohol.

If the difficulty encountered in purifying these preparations of proteose and the different methods by which they have been obtained are considered the agreement between them except

Dialysis of the aqueous extract of 100 grams of meal precipitated 16.6 grams of globulin, which was largely soluble in brine. The solution filtered from this precipitate began to coagulate on heating to about 55°; after further heating to 80° the coagulum amounted to 1.53 grams. The reactions of the aqueous extract are like those similarly obtained from other leguminous seeds and indicate that the globulin is dissolved by means of the potassium phosphates contained in the seed.

To obtain the proteids soluble in sodium chloride solution, 2000 grams of meal were treated with ten liters of ten per cent. brine, the extract was strained through fine bolting-cloth and the residue squeezed in a screw press. The turbid, gummy extract, measuring about eight liters, was centrifugated until no more solid matter could be removed. The liquid was pumped through a thick bed of filter-paper pulp and yielded a reddish yellow solution, which appeared perfectly clear by transmitted light, but was opaque by reflected light. This extract was saturated with ammonium sulphate and a very bulky precipitate obtained which, after draining on filters over night, measured, when removed from the papers, over two liters. This precipitate was stirred up with a little water, strained through bolting-cloth to break up lumps, and dialyzed in running water over night. By this process the excess of ammonium sulphate, which had prevented solution, was so far removed that the proteid completely dissolved with the help of the remaining sulphate, in about three liters of water. The liquid was then filtered perfectly clear and again dialyzed for four days. The contents of the dialyzers were then allowed to deposit the large precipitate of globulin that had separated, and from this the solution A was siphoned off. The precipitate was collected on several filters, the contents of one were thoroughly washed in succession with water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. Preparation 1, weighing 25.11 grams, was thus obtained. The rest of the globulin was allowed to drain thoroughly on the filters and then dissolved in 750 cc. of five per cent. brine, yielding 1250 cc. of solution. To this was added 1000 cc. of water and the large precipitate produced, after standing about four hours, was filtered out and without washing was treated with ten per cent. brine. Nearly all dissolved, but a very slimy sub-

stance that remained suspended in the solution, made filtration practically impossible. The solution was therefore passed

The proteid separated in spheroidal form and was filtered out, washed with water and with alcohol, making preparation 7.

A portion of preparation 4 was suspended in water and mostly dissolved by help of a little acetic acid. Dilute sodium carbonate solution was added until the proteid appeared to be completely precipitated, leaving the liquid distinctly acid to litmus. Crystallized salt was added, which gave a nearly complete solution of the precipitate. The solution was filtered and dialyzed for four days, when the precipitated globulin was filtered out, washed, and dried, giving preparation 8.

Another preparation was made from a neutralized extract, by treating 200 grams of meal with two liters of five per cent. salt solution to which had been added a quantity of baryta, previously determined to be sufficient to make the resulting extract neutral to litmus.

The mixture was strained through fine bolting-cloth and allowed to settle over night, but the suspended matter separated very imperfectly. The extract was then filtered on a pulp-filter with a pump, and 1500 cc. of a very nearly clear solution obtained, which was much less opalescent than any previously made from unneutralized extracts. This was saturated with ammonium sulphate and the resulting precipitate dissolved in water; the solution obtained was filtered perfectly clear and dialyzed for three days. The contents of the dialyzer were then filtered and the precipitate was washed with water. A portion of this substance was used to determine the reactions of this proteid and the remainder was washed with alcohol and dried, forming preparation 9.

All the preparations thus described were then dried to constant weight at  $110^{\circ}$  and analyzed with the following results :

GLYCININ; GLOBULIN OF YELLOW SOY BEAN.

	1	2	3	4	5
Carbon .....	52.04	51.73	51.84	51.94	51.90
Hydrogen .....	7.06	6.74	6.89	6.93	7.03
Nitrogen .....	17.14	17.72	17.46	17.52	17.44
Sulphur.....	0.77	0.76	0.79	0.73	0.66
Oxygen .....	22.99	23.05	23.02	22.88	22.97
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>
Ash .....	0.34	0.57	0.43	0.53	0.41

	6	7	8	9	Average
Carbon .....	51.75	51.65	51.71	52.12	51.85
Hydrogen .....	6.90	6.97	6.82	6.93	6.92
Nitrogen .....	17.03	17.63	17.57	17.53	17.45
Sulphur.....	0.67	0.66	0.61	0.79	0.72
Oxygen .....	23.65	23.09	23.29	22.63	23.06
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00
Ash .....	0.30	1.34	0.61	0.38	....

With the exception of the figures for nitrogen in the crude globulin, 1, and in the final small fraction, 6, these analyses are in close accord and give no evidence of any fractional separation. It is probable, therefore, that we have here a definite proteid distinct from legumin, containing one-half per cent. less nitrogen and three-tenths per cent. more sulphur than that substance. We propose for this globulin the name *Glycinin*. Its reactions, determined by an examination of preparation 9, are as follows:

In sodium chloride solutions it is readily soluble and is precipitated by dialysis, by dilution, and by cooling.

By dialysis or by cooling it separates in the form of spheroids which, according to circumstances, after settling from the solution either unite to a more or less coherent mass or else form a clear, transparent, viscid fluid, which, like legumin under similar conditions, is rendered white and solid by treating with water.

Solutions containing more than two per cent. of sodium chloride dissolve glycinin freely; the solvent power of those containing less salt diminishes more rapidly than the percentage of salt decreases.

Dissolved in sodium chloride solution, glycinin is not precipitated by saturating with magnesium sulphate or sodium chloride, but is completely precipitated by saturating with sodium sulphate at 34°.

In pure water, glycinin, when prepared from carefully neutralized extracts, is not soluble.

If soy bean meal is treated with water, upwards of sixteen per cent. of this globulin is dissolved, but in this case the solution is doubtless due to the potassium phosphates contained in the seed, as was pointed out in our paper on legumin.

Dissolved in ten per cent. sodium chloride solution, glycinin

is not coagulated even by prolonged heating in a boiling water-bath.

By dilute acetic acid a precipitate is formed insoluble in excess of salt solution. If, however, glycinin be dissolved in a solution containing but little salt, the precipitate produced by acetic acid is soluble in a slight excess of either acid or salt. The insoluble, so-called albuminate form of this globulin, like that of legumin, when treated with salt solution becomes gelatinous and it is impossible to filter solutions containing even a small quantity of it.

In absence of salts, glycinin is readily soluble in quite dilute acetic acid and is precipitated from such solution by sodium carbonate, even before the acid is wholly neutralized. When the acid is completely neutralized the precipitate obtained is entirely soluble in brine. Dissolved in ten per cent sodium chloride solution, glycinin is precipitated by tannic acid and by picric acid, the latter yielding a precipitate soluble in an excess of salt solution if too much picric acid be not present. With mercuric chloride no precipitate is produced. With Millon's Adamkiewicz's, the biuret and xanthoproteic test the usual proteid reactions result.

The solution A, page 420. which, as described, had been filtered from the globulin precipitated by dialyzing the solution of the ammonium sulphate precipitate of the total proteids of the extract, contained the remaining proteids extracted from the beans. This solution was saturated with ammonium sulphate, the precipitate so produced was filtered out and dissolved in a small quantity of water. After filtering clear, the solution was dialyzed for eight days. The globulin, which separated in well-formed spheroids, when washed and dried weighed twenty grams, preparation 10. The filtrate from 10 was saturated with ammonium sulphate, the precipitate dissolved in a little water, filtered clear, and dialyzed for five days; a small deposit appeared which when washed and dried weighed 2.71 grams, preparation 11. The solution filtered from 11 was returned to the dialyzer and, as nothing more separated after forty-eight hours, the dialyzer was transferred to alcohol. During the next forty-eight hours a considerable precipitate formed which when washed with alcohol and dried weighed 11.5 grams. Of this

substance seven and five-tenths grams were treated with water and the insoluble part was thoroughly washed with water and alcohol and dried. Preparation 12 was thus obtained, weighing four and seven-tenths grams. The filtrate, from the precipitation of this substance by dialysis in alcohol, was mixed with a large excess of alcohol and the precipitate caused thereby was filtered out, dehydrated with absolute alcohol, dried and found to weigh one and four-tenths grams, preparation 13. These preparations were dried at 110° and analyzed with the following results :

	10	11	12	13
Carbon.....	51.94	52.00	53.06	48.76
Hydrogen.....	6.88	6.83	6.94	6.28
Nitrogen.....	16.51	16.36	16.14	16.14
Sulphur .....	0.60	24.81	1.17	28.82
Oxygen .....	24.07		22.69	
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00
Ash .....	0.39	0.19	0.44	1.35

Of these preparations 10 and 11 have nearly the composition of phaseolin, but whether they are identical with that globulin could not be ascertained because they had become so largely coagulated by washing with alcohol and drying, that their reactions could not be satisfactorily determined.

A small quantity of globulin was obtained by further dialyzing the filtrate from preparation 9, page 422, which, when dissolved in ten per cent. salt solution, became turbid at about 95°, and after continued heating at 99°, gave a considerable coagulum. Hydrochloric or acetic acid added to its solution in ten per cent. brine gave no precipitate, and dilution with water gave a precipitate only when carried to a great extent. These reactions are characteristic of phaseolin, and taken in connection with the analyses of the similarly obtained preparations 10 and 11, make it probable that these seeds contain a small proportion of phaseolin.

Preparation 12 has the composition of legumin, which we have obtained in the same manner from a number of other leguminous seeds.

Preparation 13 is proteose.

SOY BEAN. (*Kiyusaki Diadzu*.)

Fine flour made from this variety of the soy bean was first treated with petroleum benzine and obtained nearly free from fat. By extracting 2000 grams of the flour, thus prepared, with brine and proceeding in exactly the same manner as in making preparation 1 from the yellow soy bean, a large precipitate of globulin was obtained, a part of which, when washed and dried, gave preparation 14, weighing twenty-five grams. The remainder of the globulin was drained on filters, suspended in water and 300 cc. of ten per cent. sodium chloride solution added, bringing the volume to 1000 cc. Under this treatment very nearly all dissolved. An equal volume of water was then added to the solution and the separated globulin allowed to settle. The precipitate was collected on a filter and redissolved in ten per cent. brine. The solution was filtered perfectly clear and dialyzed for forty-eight hours. The precipitate, so separated, was washed with water and with alcohol and dried, giving preparation 15, weighing 83.5 grams. The solution filtered from the first precipitation of 15, caused by dilution, as just described, was cooled to 8° during twenty-four hours. The substance thus separated, which formed a clear semifluid layer at the bottom of the jar, was thoroughly washed with water and with alcohol and dried. It weighed 12.85 grams and formed preparation 16.

After drying at 110° to constant weight these preparations were analyzed as follows:

## GLYCININ.

	14	15	16	Average.
Carbon.....	51.80	52.15	52.09	52.01
Hydrogen.....	6.93	6.87	6.86	6.89
Nitrogen.....	17.45	17.48	17.47	17.47
Sulphur .....	0.75	0.72	0.70	0.72
Oxygen ....	23.07	22.78	22.88	22.91
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00
Ash .....	0.39	0.42	0.28	

These results agree well with those obtained from the yellow soy bean.



GLYCININ.

	Yellow Soy bean.	Kiyusuki diadem Soy bean.
Carbon .....	51.85	52.01
Hydrogen .....	6.92	6.89
Nitrogen .....	17.45	17.47
Sulphur .....	0.72	0.72
Oxygen .....	23.06	22.91
	<hr/> 100.00	<hr/> 100.00

CONCLUSION.

The soy bean contains as its chief proteid constituent *glycinin*, a globulin similar in properties to legumin, but of somewhat different composition, containing nearly twice as much sulphur, four-tenths per cent. more carbon, and one-half per cent. less nitrogen.

We give as the composition of this proteid the results of our analysis of preparation 9, which was obtained from a neutral and perfectly clear extract, for we believe that this represents more accurately the true composition of *glycinin* than the average of all the preparations.

GLYCININ.

Carbon.....	52.12
Hydrogen.....	6.93
Nitrogen.....	17.53
Sulphur.....	0.79
Oxygen .....	22.63
	<hr/> 100.00

The soy bean contains a more soluble globulin which resembles phaseolin in composition, and, so far as we could ascertain, also in its reactions. The amount of this proteid is small and the evidence that it is in reality phaseolin was not wholly satisfactory.

## LEGUMELIX.

Carbon .....	53.06
Hydrogen .....	6.94
Nitrogen .....	16.14
Sulphur .....	1.17
Oxygen .....	22.69
	<hr/>
	100.00

A small quantity of proteose was also obtained from the soy bean having the following composition :

## PROTEOSE.

Carbon .....	48.76
Hydrogen .....	6.28
Nitrogen .....	16.14
Sulphur )	28.82
Oxygen )	
	<hr/>
	100.00

Owing to the small amount of proteose no evidence was obtained as to the purity or individuality of this preparation.

## ELECTRICAL DISTURBANCE IN WEIGHING.

BY H. K. MILLER.

Received February 28, 1898.

WHILE making some fat determinations, I found a practice, which I believe is quite common among chemists, to be the source of quite serious errors. The practice is that of wiping a flask with a dry cloth just previous to weighing it. In making a second weighing of a flask containing an oil which had been extracted from a sample, I was very much surprised to find a considerable increase over the weight first obtained.

The first idea that presented itself was that the oil had suffered oxidation during the second heating, but this idea was dispelled when to my greater surprise a third weighing showed the flask and contents to weigh even less than at first. Careful experiments led to the conclusion that in wiping the flask it became electrified, and that this static charge, acting on the floor of the balance, induced on it a charge of opposite character, and that the mutual attraction between these two charges of electricity had the effect of apparently increasing the weight of the flask.

The potential of the charge would vary with the atmospheric conditions and with the manner of wiping the flask. By using a linen cloth in very dry weather, it was found possible to produce a charge on a 100 cc.-flask which would require 0.08 gram additional weight to restore equilibrium.

A high charge like this, however, would be rapidly dissipated and the flask would appear to lose weight. It was found that a charge which apparently caused an increase in weight of about 0.01 gram would be retained quite a long time, and one might readily overlook the error which would be thus introduced. It was further found that a small charge would be retained many days on a flask kept in a desiccator. In damp weather a charge would readily pass off and not give rise to an error, but on a very dry day the practice of wiping glassware just before weighing is liable to cause serious errors.

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## ANALYTICAL NOTES UPON THE ESTIMATION OF PHOSPHORUS IN STEEL.<sup>1</sup>

BY R. W. MAHON.

Received March 4, 1898.

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<sup>1</sup> In this paper I have recorded a number of experiments upon the estimation of phosphorus in steel. Their subject is a study in detail of the molybdate-magnesia method. Some of the experiments are upon properties of the molybdate precipitate, which are not connected with this method for estimating phosphorus. The concluding pages describe precipitation of phosphoric acid, out of measured quantities of a standard solution of sodium phosphate.

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THESE experiments were made with steel of low carbon content (below 0.10). The preparation of the solutions of the steel for the molybdate precipitation applies to soft steel. The remainder is of general application in steel analysis. These steels do not contain arsenic, and I have not considered the separation of arsenic and phosphorus, except incidentally.

#### THE SAMPLES.

A volume of liquid steel is throughout of practically uniform composition, and the percentage of phosphorus in all parts of it is the same.

#### LADLE TESTS FROM A TWENTY THOUSAND POUNDS HEAT OF BESSEMER STEEL, WHICH WAS POURED INTO THREE MOLDS.

Test number.	Percentage of phosphorus.	Remarks.
1.....	0.096 (average)	Sample taken as the steel was about to be poured into the second mold.
2.....	0.100	" About to be poured into the third mold.
3.....	0.098	" Third mold nearly full.
1.....	0.098	} Another example.
2.....	0.102	
3.....	0.102	
4.....	0.102	

On the other hand, it is sometimes difficult to obtain drillings from a billet or finished shape, which accurately represent the composition. Incorrect opinions have doubtless been drawn of the relation between physical properties and chemical composition, and also with regard to the accuracy of methods, from neglect to remember the facts of segregation. The four samples of steel employed in this work were planed from the surface of billets, rejecting the first portion. The planings from sample No. 1 were mixed and bottled. The others were prepared as follows: The planings were sieved in a coffee strainer, the

dust rejected, and the remainder mixed and bottled. The dust for each was about one-twenty-sixth of the whole. Estimations of phosphorus in drillings, made at about twelve places on the surface of the billet from which sample No. 1 was planed, showed that segregation had taken place to a limited extent.

#### ESTIMATIONS OF PHOSPHORUS IN THE DUST AND COARSER PARTICLES.

Sample number.	Percentage of phosphorus.	
	Coarser planings, average.	The dust, average.
2 .....	0.103	0.109
3 .....	0.101	0.100
4 .....	0.108	0.111

The determinations in different parts of the fluid mass, and in the particles of different size planed from billet surfaces, were made by titration of ammonium phosphomolybdate with potash solution. As the point of the plane passes over a portion of the surface at which phosphorus has segregated, more dust is formed than from the remainder of the surface, which is softer and less brittle, and the dust sifted out will be higher in phosphorus, if there is segregation upon the surface. That the more brittle portions of a surface will yield the larger proportion of dust is evident; it has also been referred to by Von Jüptner<sup>1</sup>, who quotes experiments of Leopold Schneider.

In spite of slight segregation on some of the surfaces from which samples were planed, they are regarded as fairly uniform owing to their subsequent treatment. This applies to all of the samples but No. 1. I have been able to use some of the results from No. 1, but not all. Continued tilting of the jar containing the sample, concentrated the dust at the bottom. Removal of the fine portion would not appreciably change the percentage of phosphorus, but concentration to three times the original amount would raise the percentage of phosphorus 0.001 per cent., assuming that the phosphorus in both coarse and fine portions for samples Nos. 1 and 2 are the same, both having been planed from the same face.

#### PROOF FOR ACCURACY OF PROCESS.

After obtaining a solution of the sample in nitric acid and oxidizing it, it is possible to determine the accuracy of the

phosphate again through the cycle of operations which were performed in the analysis. I have done this and recorded the results in the following table. Each weight of magnesium pyrophosphate used to calculate a percentage of phosphorus mentioned in the table was corrected by fusing with alkaline carbonates, extracting with water and acid, and evaporating to dryness, taking up with acid, and filtering. The residue was the correction, and the filtrate was used for the reprecipitation of ammonium phosphomolybdate. This method of correcting the weight is not the best way, giving corrections slightly too small. It is also unnecessarily tedious. It was used in these few experiments in order to reconvert pyrophosphate into orthophosphate. The carbonates were examined for phosphorus with negative results.

Results Nos. 1, 2, and 3, of column 3, were obtained by titrating ammonium phosphomolybdate precipitates which had been washed with cold water, with potash solution. The precipitates were thrown down from the solution of the orthophosphate obtained as described above. Its acid solution was rendered alkaline by ammonia and then acid by nitric acid, and molybdate solution added at proper temperature. Although these results were satisfactory, others were obtained in which the large quantity of the salts of the fixed alkalies appeared to interfere with success. I therefore performed the experiments of which the results are recorded in the 4th, 5th, and 6th places of column 3. Here each solution was treated with ferric chloride<sup>1</sup> and after a basic acetate precipitation, a solution was prepared from the precipitate by solution in hydrochloric acid which was then employed for the molybdate precipitation after neutralization as in the previous examples. These later molybdate precipitations were always satisfactory. In these also the estimation was made by titration with potash solution. Results 7 and 8, in column 3, were obtained as follows: The weights of magnesium pyrophosphate from which (corrected) the results 7 and 8 of column 2 were calculated, having been fused with alkaline carbonates and solutions prepared from the fusions as described, basic acetate precipitations and then molybdate precipita-

<sup>1</sup> The amount of ferric chloride used was such that a sum of less than 0.0002 per cent. of phosphorus for ten grams of sample was introduced.

tions were made as described for 4, 5, and 6. In the solution of the molybdate precipitate in ammonia, the phosphorus was precipitated as magnesium ammonium phosphate and finally weighed as before as pyrophosphate, finding a correction to be applied for impurity present, as in the first pyrophosphate. The treatment of the solution of the molybdate precipitate in ammonia, for separation of the trace of iron present in the colloidal state, and the adjustment of the other details necessary to accurate precipitation of magnesium ammonium phosphate, both here and for the first precipitate are identical in all essentials with those employed in estimations giving accurate results, recorded in the longer tables. These details will be described.

The following table contains eight determinations of phosphorus in a sample of steel by the molybdate-magnesia method, and eight re-determinations, using the weights of pyrophosphate as starting-points.

Number of the determination.	Percentage of phosphorus by the molybdate-magnesia method.	Redeterminations using the weights of magnesium pyrophosphate as starting-points.	Remarks.
1 .....	0.104	0.103	By precipitation as ammonium phosphomolybdate, out of the solution of the fusion of the phosphate.
2 .....	0.104	0.102	
3 .....	1.102	0.101	
4 .....	0.103	0.103	By the same method as the first three preceded by a precipitation with basic ferric acetate.
5 .....	0.104	0.103	
6 .....	0.103	0.101	
7 .....	0.102	0.101	By the same method as last three, followed by solution in ammonia, and precipitation with magnesia mixture.
8 .....	0.104	0.102	

I have determined the phosphorus frequently in this sample and consider it to be 0.103. The molybdate-magnesia method may be considered as proceeding to its end in the three following steps:

1. OBTAINING A SOLUTION FROM THE STEEL OF AMMONIUM PHOSPHATE CONTAINING ALL THE PHOSPHORUS AND ONLY A FAINT TRACE OF IRON.

precipitation as ammonium phosphomolybdate, proceed upon two assumptions: (1) that no phosphorus escapes during solution and (2) that it is all obtained in a precipitable form. It needs only a simple experiment to convince one's self of the fact that nitric acid of 1.135 sp. gr. proposed for use in steel analysis by Drown,<sup>1</sup> dissolves steel without evolution of hydrogen phosphide. I have made such an experiment, and after passing the gases through silver nitrate have made an examination for phosphoric acid with negative result. The nature of the reaction between silver nitrate and hydrogen phosphide is not unknown to us and indeed Von Jüptner<sup>2</sup> has recently familiarized us with it, through his experiments upon a possible difference of the mode of occurrence of phosphorus in steel, using the precipitated silver as a measure of the hydrogen phosphide given off by the action of dilute sulphuric acid on the steel. I have preferred to examine the absorbing solution (after suitable preparation) by the addition of ammonium molybdate.

On the other hand the second assumption upon which the determination of phosphorus in steel rests, namely that all of the phosphorus in the solution of the steel can be obtained in a precipitable form, is not so easy of proof, and indeed in its nature may be regarded as incapable of absolute proof. It can only be affirmed of a given method for preparing a solution of steel for precipitation that it yields the highest percentage of phosphorus, which is obtained by any other procedure. It does not follow that all of the phosphorus in the sample has been obtained. This latter statement could only be made after having made a compound of given content in phosphorus and obtaining the known result by analysis. To complete the proof the compound must have been made in the same manner: in fact it would be steel, and absolutely homogeneous. These are conditions impossible of fulfilment. The statement that all of the phosphorus in the sample had been obtained, could be made only after getting the same result by difference. This presupposes methods for determining the remaining constituents so delicate as to admit of this, a condition to which the art of analysis has not yet attained.

<sup>1</sup> *Trans. Am. Inst. Min. Eng.*, 18, 90.

<sup>2</sup> *J. Iron and Steel Inst.*, 1897, No. 1, 224.



*Oxidation.*—In preparing a steel for precipitation of its phosphorus, after solution in dilute nitric acid, by oxidation, the various oxidants are of unequal value. The experiments in the following table are not to show the impossibility of oxidizing mild steels by the several means mentioned, but only the relative difficulty when compared with potassium permanganate. It is possible that in most of the cases, perhaps in all, the oxidation would be perfect were the action sufficiently long continued, or a sufficiently large amount of the oxidizer used, or if both these conditions were favorable. In each of the experiments of the table, four grams of steel were boiled in seventy cc. of water and thirty cc. of nitric acid (sp. gr. 1.42). The oxidation in question was then attempted, the solution afterwards made ammoniacal and then just acid by nitric acid, and fifty cc. of molybdate solution added to the solution, which was at 75° C. The precipitates were titrated with potash solution.

THE EFFECT OF VARIOUS OXIDANTS UPON THE DILUTE NITRIC ACID  
SOLUTION OF A STEEL WHOSE PERCENTAGE OF PHOSPHORUS  
IS 0.108.

Additional means of oxidation, besides the nitric acid em- ployed for solutions of the sample.	Percent- age of phos- phorus.	Remarks.
None.....	0.060	The solution was boiled a short time.
".....	0.060	The solution was boiled a short time.
".....	0.075	The solution was boiled a long time.
Hydrochloric acid.....	0.081	The solution boiled, hydrochloric acid
".....	0.085	added and again boiled.
Potassium chlorate.....	....	A small quantity of the crystals. A very defective precipitation.
Potassium chlorate and hydrochloric acid.....	0.107	{ Thirteen grams of crystals. Hydro- chloric acid to dissolve precipitated oxides of manganese.
Bromine water.....	0.073	
".....	0.062	
Sodium peroxide.....	0.083	A considerable quantity of the solid substance.
Hydrogen dioxide.....	0.084	A few cc.; strength unknown.
Hydrogen dioxide and hy- drochloric acid.....	0.090	Added alternately in small quantities.
Hydrogen dioxide.....	0.109	Sixty cc.; a few cc. at each addition.
Chromic acid.....	0.094	A few cc. of nitric acid, sp. gr. 1.42, saturated with chromic acid.
Potassium bichromate....	0.079	A few cc. of water, saturated with potassium bichromate.
Baked on steam-bath for several days at about 80°C.	{ 0.108 } { 0.107 }	Taken up with hydrochloric acid, and boiled down; then boiled down twice with nitric acid.

*Precipitation of Ammonium Phosphomolybdate.*—Each of the determinations by the molybdate-magnesia method was made upon ten grams, in two quantities of five grams each. Shimer<sup>1</sup> originally evaporated the solution, after solution of the steel, oxidation by potassium permanganate, and solution of the precipitated oxides in hydrochloric acid, using the filtrate from the silicon determination for phosphorus. The first published reference to the use of hydrochloric acid for dissolving the oxides of manganese, followed without evaporation by neutralization with ammonia,

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<sup>1</sup> *Am. Ins.*

<sup>2</sup> *Stahl un*

<sup>3</sup> *Ztschr. d*

<sup>4</sup> *Ibid.*, 3,

tions there were approximately thirty grams of nitric acid ( $\text{HNO}_3$ ) present. In (B) fifteen grams approximately.

Fresenius' well-known molybdate solution recipe—molybdic acid one part, ammonia of 0.96 sp. gr. four parts, and nitric acid of 1.20 sp. gr. fifteen parts—is the one used in my experiments; *viz.*, molybdic acid 100 grams, ammonia of 0.90 sp. gr. 200 cc.,

method A, as reported in the paper above referred to. This depends on some molybdate being carried down with the precipitate. The cause of this is its rapid formation, enclosing molybdate, and not on account of the precipitation of molybdic acid as such. The precipitation of molybdic acid is seen when the molybdate solution and ammonia mixture is rapidly poured into the solution of the steel, the latter being at a temperature of  $105^{\circ}\text{C}$ ., without taking pains to direct the stream into the center. Where it runs down the sides of the flask into the solution, molybdic acid is seen to separate in quantity and again to go into solution when the flask is agitated, leaving a clear solution, out of which ammonium phosphomolybdate precipitates.

That B gives slightly higher results than A when titrating with potash solution, does not necessarily arise from more molybdate present in the precipitates in the first case. The cause might be, it is possible to imagine, a molecule formed with more free acid content, hydrochloric or nitric, than the two molecules mentioned by Hundeshagen.<sup>1</sup> It can, however, be shown that the difference arises from the first cause, by estimations of phosphorus in a standard steel, using three methods, and employing precipitates formed in both ways.

TABLE EXPLAINING THE DIFFERENCE OF RESULTS BY A AND B.

	By caustic potash	By weight of precipitate, dried at $110^{\circ}\text{C}$ .	By potassium permanganate.
A.....	0.108	{ 0.108 0.109	0.109 0.109
B.....	0.110	{ 0.112 0.110	0.112 0.110

The difference in percentage of phosphorus found by direct treatment of molybdate precipitate is not dependent, however, upon the difference in the method of neutralization employed, but upon the temperature of precipitation, as can be proved by precipitating at  $105^{\circ}\text{C}$ . after neutralization in the older way, and after neutralization in the newer way by precipitating at  $75^{\circ}\text{C}$ .

	Temperature of precipitation	Percentage of phosphorus found.
Old method of neutralization ..	$105^{\circ}\text{C}$ .	0.111
New " " " ..	$75^{\circ}\text{C}$ .	0.108

<sup>1</sup> *Loc. cit.*

## WASHING AMMONIUM PHOSPHOMOLYBDATE.

Number.	Percentage of phosphorus found. <sup>1</sup>	True percentage of phosphorus.	Method of precipitation.	The washing.
1	0.107	0.108	A	850 cc. of cold water.
2	0.105	0.108	A	850 cc. " " "
3	0.107	0.110	B	1000 cc. " " "
4	0.107	0.110	B	1000 cc. " " "
5	0.062	0.108	A	1125 cc. " two per cent. nitric acid.
6	0.039	0.108	A	1125 cc. " two per cent. nitric acid and then with 110 cc. of cold water.
7	0.097	0.110	B	75 cc. of cold water, then 1000 cc. of two per cent. nitric acid, then 200 cc. cold water.
8	0.091	0.110	B	225 cc. of cold water, then 1000 cc. of two per cent. nitric acid, then 300 cc. cold water.
9	0.108	0.108	A	200 cc. of two per cent. nitric acid, then 75 cc. cold water.

These were made with the same sample, and 0.108 and 0.110 denote the results of accurate determinations when titrating precipitates obtained by methods A and B respectively.

Isbert and Stutzer<sup>1</sup> first used cold water to wash the molybdate precipitate. Their results show no loss when washing with 500 cc., and but a slight loss when one liter is used. See Nos. 1 to 4 inclusive, in which the results are slightly lower than those obtained by washing with one-fifth or one-fourth of the mentioned quantities, as in an actual estimation. It was only in preparing precipitates for titration with potash solution that water was the washing fluid.

In dilute nitric acid the molybdate precipitate is much more soluble. (See No. 5.) In this one an empty paper was washed with the same washing fluid, and the result used as a correction.

When a copious washing with nitric acid is followed by a washing with water, the solubility is even more marked; in the latter case being accompanied by a visible running of some of the precipitate through the paper. (See Nos. 6 to 8 inclusive.) These figures are evidently not the result of simple solution, but of decomposition from prolonged washing, a decomposition

<sup>1</sup> *Ztschr. anal. Chem.*, 26, 584.

rendered more apparent and perhaps increased by subsequently washing with water. Otherwise washing in moderation with dilute nitric acid would dissolve less than in the foregoing examples, but a still appreciable quantity of the precipitate. Actually, washing in moderation with two per cent. nitric acid, does not dissolve any of the precipitate. (See No. 9.) Two hundred cc. of dilute nitric acid is an unnecessarily large quantity to employ.

*Re-solution of Molybdate Precipitate.*—The absolute separation of small quantities of phosphorus and large quantities of iron by one precipitation of ammonium phosphomolybdate, washing with dilute nitric acid is impossible.

WEIGHTS OF FERRIC OXIDE RETAINED BY THE PRECIPITATE FROM FIVE GRAMS OF STEEL.

Precipitation.	Weights of ferric oxide.
A { 1	0.0016
2	0.0017
B { 1	0.0015
2	0.0015

This iron present in the colloidal condition in the ammoniacal solution of the molybdate precipitate separating upon evaporation, and carries down with it about two-tenths of a milligram of phosphorus in these steels. It is my custom to filter at this point,<sup>1</sup> redissolve the iron in hydrochloric acid, make its solution ammoniacal, and then faintly acid with nitric acid; now add a few cc. of molybdate solution. The small precipitate having been filtered and redissolved in ammonia, its solution running into the main quantity of ammonium phosphate, this is to be evaporated, until the smell of ammonia has disappeared and the bulk is sufficiently reduced.

The solution is now prepared for precipitation by adding the quantity of hydrochloric acid required for the particular case, and then ammonia from a burette, finally obtaining a faintly ammoniacal solution which is diluted to the volume wished, and magnesia mixture dropped in, with constant stirring, followed by the addition of ammonia in the same manner.<sup>2</sup>

<sup>1</sup> It is impossible to give an intelligible description of experiments upon this theme without mentioning familiar details.

<sup>2</sup> Blair's Chemical Analysis of Iron, First Edition, p. 82, prescribes the addition of strong ammonia, in the proportion of one-fourth of the final volume. Such a solution

## II. THE ACCURATE PRECIPITATION OF PHOSPHORUS AS MAGNESIUM AMMONIUM PHOSPHATE.

*The use of magnesium chloride, ammonium chloride, and ammonia.* The same washing fluid was used throughout: ammonia of 7.25 per cent. (that is, water three volumes, ammonia, sp. gr. 0.90, one volume) unless otherwise mentioned.

Two magnesia mixtures were used. The first was made from magnesia, hydrochloric acid, and ammonia, and the magnesium chloride and ammonium chloride per cc. determined. This mixture is called 1, in the tables. The second magnesia mixture called 2 in the tables, is described on page 51 of "Blair's Chemical Analysis of Iron," first edition. Fifty-eight grams of ammonium chloride in two liters were used instead of the quantity called for by that recipe.

### MAGNESIA MIXTURE, CONTAINING ENOUGH AMMONIA TO IMPART A DECIDED ODOR.

	No. 1.	No. 2.
Magnesium Chloride, crystallized.....	66 grams.	110 grams.
Ammonium Chloride.....	69 "	38 "
Volume.....	2 liters.	2 liters.

contains 7.25 per cent. of free ammonia ( $\text{NH}_3$ ). This is the amount of ammonia added in each of the following experiments, unless otherwise mentioned. Two and five-tenths per cent. of free ammonia ( $\text{NH}_3$ ) in solution and for wash is probably most used for this precipitate—Fresenius' Quantitative Analysis; Fresenius: *Ztschr. anal. Chem.*, 6, 403; Wagner and his coworkers. *Ibid* 19, 444 and 21, 353; etc. It is the strength used in the official method for agricultural analysis in Germany, and is described in Bulletin 46, U. S. Department of Agriculture as part of the official method for agricultural anal-

THE USE OF MAGNESIUM CHLORIDE, AMMONIUM CHLORIDE, AND  
AMMONIA.

Number of the estimation.	Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Magnesia mixture used.	Remarks.
1	1	0.104	0.043	0.57	0.010	60	125	1	Magnesium chloride in small excess. Small quantity of ammonium chloride present.
2	1	0.103	0.043	0.57	0.007	76	120	1	
3	1	0.102	0.043	1.07	0.014	76	120	1	
4	1	0.104	0.043	1.42	0.019	76	90	1	
5	3	0.100	0.086	1.14	0.021	54	128	1	
6	3	0.101	0.086	1.14	0.018	62	128	1	
7	3	0.101	0.086	1.14	0.017	69	126	1	
8	3	0.099	0.058	0.99	0.016	60	105	1	
9	3	0.100	0.086	1.14	0.019	60	130	1	
10	3	0.103	0.086	1.14	0.019	60	125	1	
11	3	0.100	0.058	0.99	0.016	60	130	1	
12	4	0.108	0.077	0.70	0.023	30	110	2	
13	4	0.108	0.077	0.70	0.008	87	100	2	
14	4	0.114	0.090	0.10	0.002	60	120	2	
15	4	0.117	0.090	0.10	0.002	60	120	2	
16	1	0.103	0.043	9.57	0.124	77	98	1	Magnesium chloride in small excess. Moderate quantity of ammonium chloride present.
17	1	0.101	0.043	5.92	0.099	60	130	1	
18	1	0.103	0.043	5.92	0.099	60	130	1	
19	1	0.102	0.043	5.92	0.099	60	130	1	
20	1	0.104	0.043	5.92	0.099	60	130	1	
21	1	0.104	0.043	5.91	0.089	67	130	1	
22	2	0.102	0.043	6.25	0.142	60	112	1	
23	2	0.101	0.043	6.25	0.142	60	112	1	
24	2	0.102	0.043	6.25	0.142	60	112	1	
25	3	0.100	0.086	5.15	0.067	77	147	1	
26	3	0.100	0.086	5.15	0.067	77	144	1	
27	3	0.100	0.058	11.00	0.138	80	120	1	
28	3	0.099	0.058	11.00	0.130	80	130	1	
29	4	0.106	0.077	10.79	0.135	80	100	2	
30	4	0.109	0.077	10.79	0.124	87	138	2	
31	4	0.109	0.077	25.79	0.143	180	110	2	Magnesium chloride in small excess. Large quantity of ammonium chloride present.
32	4	0.109	0.077	25.79	0.143	180	110	2	
33	4	0.116	0.255	1.00	0.025	41	110	2	Magnesium chloride in large excess. Small quantity of ammonium chloride present.
34	4	0.111	0.180	1.65	0.025	57	110	1	
35	4	0.111	0.180	1.65	0.025	60	110	1	



36	4	0.114	0.255	10.00	0.105	95	110	2	Magnesium chloride in large excess. Moderate quantity of ammonium chloride present.
37	4	0.110	0.255	10.00	0.097	103	110	2	
38	3	0.100	0.180	10.18	0.087	117	137	1	
39	3	0.103	0.180	10.18	0.085	120	115	1	
40	3	0.103	0.180	11.00	0.103	107	108	1	
41	3	0.099	0.180	11.00	0.103	107	118	1	Magnesium chloride in large excess. Large quantity of ammonium chloride present.
42	4	0.110	0.255	25.00	0.170	153	140	2	
43	4	0.110	0.255	25.00	0.170	153	140	2	
44	2	0.104	0.130	6.00	0.081	74	90	1	Use of ammonia of 2.5 per cent. in solution of customary size.
45	2	0.102	0.130	6.00	0.090	67	90	1	
46	2	0.104	0.130	6.00	0.090	67	90	1	
47	4	0.101	0.077	20.00	0.070	288	115	2	Large volume for precipitation. Percentage of ammonia 2.5
48	4	0.111	0.077	0.80	0.003	288	110	2	
49	4	0.105	0.281	20.00	0.070	288	115	2	
50	4	0.112	0.077	0.80	0.003	288	110	2	Large volume for precipitation.
51	4	0.119	0.077	0.80	0.003	288	110	2	
52	4	0.111	0.077	10.00	0.035	288	100	2	
53	4	0.105	0.077	10.00	0.035	288	100	2	
54	1	0.098	0.043	25.00	0.104	240	100	1	
55	1	0.100	0.043	25.00	0.104	240	100	1	
56	4	0.101	0.077	20.00	0.070	288	77	2	
57	4	0.103	0.077	20.00	0.070	288	117	2	
58	4	0.110	0.255	10.00	0.035	288	100	2	
59	4	0.111	0.255	10.00	0.035	288	100	2	
60	4	0.105	0.255	20.00	0.070	288	92	2	
61	4	0.106	0.255	20.00	0.070	288	72	2	
62	4	0.109	0.077	5.00	0.083	60	110	2	
63	4	0.107	0.077	5.00	0.083	60	125	2	
64	4	0.111	0.077	5.00	0.083	60	110	2	
65	4	0.107	0.306	6.00	0.084	71	155	2	
66	4	0.107	0.306	6.00	0.084	71	125	2	
67	4	0.107	0.077	5.60	0.093	60	140	2	Magnesium chloride added as in last five. Time of precipitation, 67 and 68—2 hours, 69 and 70.—1 hour.
68	4	0.107	0.077	5.60	0.093	60	140	2	
69	4	0.110	0.306	5.90	0.077	77	130	2	
70	4	0.110	0.306	5.90	0.077	77	130	2	
71	.	0.0014	0.043	6.00	.....	60	150	.	Precipitated in 30 minutes.
72	.	0.0032	0.043	6.00	.....	60	165	.	
73	.	0.0026	0.043	6.00	.....	60	170	.	
74	.	0.0024	0.043	6.00	.....	60	110	.	Precipitated in 1 hour.
75	.	0.0014	0.043	6.00	.....	60	110	.	
76	.	0.0026	0.043	6.00	.....	60	110	.	

When magnesium chloride is used in small excess, the result is practically the same, whether ammonium chloride be present in small, moderate, or large quantity. Thus for samples Nos. 1, 3, and 4, the means are :

1.	3.	4.	Sample number.				
0.1033	0.1006	0.1080 <sup>1</sup>	Small quantity	of ammonium chloride	present.		
0.1028	0.0998	0.1075	Moderate	"	"	"	"
.....	.....	0.1090	Large	"	"	"	"

Error can however occur when using magnesium chloride in small excess if the amount of ammonium chloride be sufficiently reduced. Estimations Nos. 14 and 15, on sample No. 4, show 0.114 and 0.117.

When magnesium chloride is added in large excess error is more frequently introduced. Thus for samples Nos. 3 and 4, the means are :

3.	4.	Sample number.				
.....	0.1127	Small quantity	of ammonium chloride	present.		
0.1013	0.1120	Moderate	"	"	"	"
.....	0.1100	Large	"	"	"	"

The figures above for sample No. 4 also show the lessening of plus error brought about by the presence of ammonium chloride in proper quantity.

The larger the excess of magnesium chloride the more rapid the precipitation, and the more ammonium chloride present the slower the precipitation. As too great rapidity causes inaccuracy, and as ammonium chloride solution has a solvent action upon magnesium ammonium phosphate, it follows that these ingredients must be adjusted within certain limits. In other words, the proper amount of ammonium chloride is dependent upon the excess of magnesium chloride used. That the same amount of ammonium chloride does not prevent plus error irrespective of the excess of magnesium chloride is illustrated by estimation Nos. 36 to 41. Nos. 36 and 37 give a mean of 0.112 instead of the true percentage 0.108. Nos. 38 to 41 inclusive give a mean of 0.101 instead of 0.100. Here the amounts of ammonium chloride are nearly equal, and the magnesium chloride in excess, much greater for Nos. 36 and 37. All the results thus far discussed will be seen by a reference to

<sup>1</sup> Nos. 14 and 15 are not included.

the table to have been obtained when precipitating in solutions of customary size. Estimations Nos. 50 to 61 inclusive were made, effecting the precipitation in large solution. These estimations include examples with small and large excess of magnesia mixture, in presence of ammonium chloride in varied amount. Although useless as suggestions for analysis, they are interesting as showing the variations caused by variations in magnesium chloride and ammonium chloride. Detailed comment is unnecessary; the dissolving effect of ammonium chloride is a chief feature, increasing with the concentration, and lessening with the excess of magnesium chloride. By an exact balance, accurate results would be obtained. But this is uncertain of attainment, and in the twelve examples considered, has not been reached in one. Either the ammonium salt solution was too concentrated for the excess of magnesia and some weight of precipitate was dissolved or the concentration of ammonium salt solution was too slight and the precipitate was contaminated by the excess of the precipitant.

Indeed in Nos. 52 and 53, supposed to be executed identically, accidental variation has caused one to fall above and the other below the truth.

	Percentage of phosphorus
No. 52.....	0.111
" 53.....	0.105
True percentage.....	0.108

Comparisons of Nos. 50 and 51 with No. 13, and then with Nos. 14 and 15 show that it is not the weight alone, but also the concentration of the solution of ammonium chloride which prevents coprecipitation of magnesia.

Number of the estimation.	Percentage of phosphorus.	Ammonium chloride present Gram.	Ammonium chloride per cc. Gram.
50	0.112	0.80	0.003
51	0.119	0.80	0.003
13	0.108	0.70	0.008

cases, showing this to be unnecessary. The method was: boiling down until ammonia was driven off, acidifying and adding a few cc. of molybdate solution. One-tenth of a milligram of phosphorus can be detected thus, as can be seen by examining a blank, to which this quantity of phosphorus had been added, as sodium phosphate.

The filtrates from some of the twelve just described, were examined for phosphorus, with the following results:

	50	51	57	58	59	60	61
Percentage of phosphorus in the filtrate .....	0.000	0.000	0.007	0.000	0.000	0.004	0.001

Nos. 44 to 49 inclusive describe estimations, where the percentage of ammonia is two and five-tenths in the solutions for precipitation. Nos. 44, 45, and 46 give a mean of 0.1033; Nos. 22, 23, and 24 give 0.1017. The first slightly higher, on account of greater excess of precipitant, and a lesser concentration of ammonium chloride, and showing no result from lesser strength of ammonia. The latter mean is correct, and the first has a plus error of 0.0016. Approximately the same relations (except that the same strength of ammonia is present in the estimations now to be compared) exist between Nos. 38 to 41 inclusive, and Nos. 27 and 28.

Nos. 47 to 49 inclusive, like Nos. 50 to 61 inclusive, were obtained by precipitating in large volume. The same idea of variations in the amount of precipitant and of ammonium chloride, is carried out here. The results, like the corresponding ones in the other series, show no variations due to difference of strength of ammonia present.

No. 47, 0.101	No. 48, 0.111	No. 49, 0.105
" 56, 0.101	" 50, 0.112	" 60, 0.105

Nos. 62 to 66 inclusive give results obtained by adding magnesia mixture even slower than in previous cases, as follows: something more than the theoretical amount, dropped slowly in as usual and the remainder added in the same manner after an interval.

No average difference between properly made previous determinations, and Nos. 62 to 66 inclusive, is apparent.

The time of precipitation is part of the general subject of use of

magnesium chloride and ammonium chloride, for it depends upon the quantities of those salts present.

Nos. 67 to 70 inclusive illustrate the effect of excess of magnesium chloride in hastening precipitation. While Nos. 67 and 68 are slightly below the true percentage, in Nos. 69 and 70 while perfect precipitation was obtained in one hour, the precipitant was dropped in, apparently, somewhat too rapidly. But the effect of magnesium chloride in hastening and of ammonium chloride in retarding precipitation is a visible result, which I have often observed in carrying out a number of estimations simultaneously, with these details differing. In Nos. 71 to 76 inclusive, I have only recorded the phosphorus found in the filtrates.

### III. OBTAINING THE CORRECT WEIGHT OF MAGNESIUM PYROPHOSPHATE.

Eleven cm. filter-paper seems to be preferable to a smaller size, for the magnesium ammonium phosphate filtration, particles of the precipitate being less liable to crawl above its edge. The dangerous operation of drying, and burning the paper separately, should be abandoned, in favor of enfolding the precipitate in its still slightly moist paper, and burning in an inclined crucible without lid. I always use the end of a stout platinum wire to break up the precipitate, after the carbon of the paper is almost consumed. This operation can be so carried out as to give rise to no error. There are always three impurities in the magnesium pyrophosphate. These are silica, ferric oxide, and molybdic acid; the last if the precipitation has been made in presence of molybdic acid. Silica and ferric oxide are best separated by hot, very dilute hydrochloric acid. Every precipitate derived from steel was corrected for these impurities. Their sum is usually a fraction of one milligram. The weight of molybdic acid, after ignition before the blast-lamp, can be neglected.<sup>1</sup>

<sup>1</sup> Drown, in a paper by George E. Thackray, "A Comparison of Recent Phosphorus Determinations in Steel," *Trans. Amer. Inst. Min. Eng.*, October, 1895, describes his method of making two phosphorus determinations, published in the paper. The following is a part of the description: "Dissolve the ammonium magnesium phosphate in hydrochloric acid and into this solution pass sulphuretted hydrogen for three or four hours, the liquid being nearly boiling the greater part of the time. After filtering off the molybdenum sulphide, and any arsenic which may be present, the ammonium magnesium phosphate is again precipitated by ammonia, with the addition of a little more magnesia mixture." Three determinations of phosphorus in sample No. 4, carried out as I describe them, the first precipitate of magnesium ammonium phosphate being redissolved and treated according to the above quotation resulted as follows: 0.109, 0.108, and 0.109.

It is one or two-tenths of a milligram. I have determined molybdic acid in these precipitates, in the filtrate from silica and iron, by precipitating by hydrogen sulphide. Two of these were filtered and weighed on asbestos felt in a Gooch crucible, after drying, proving to be a small, doubtful fraction of one milligram. Other precipitates of this impurity by hydrogen sulphide were simply observed. A solution was prepared from forty milligrams of molybdic acid in a little ammonia, and this diluted to one liter. Portions of this were measured off, acidified with hydrochloric acid and having been diluted, treated with hydrogen sulphide gas. The quantity of molybdic acid in ten cc. of this solution if present in a pyrophosphate after ignition before the blast-lamp, would cause an error of 0.001 per cent. phosphorus for ten grams of steel. Ten cc. of the solution however if precipitated as above, give a precipitate, much greater than any derived from these pyrophosphates.

Another way of studying this subject is shown in the estimations carried out with standard sodium phosphate solution, described further on, where the error arising from presence of molybdic acid in the ignited precipitate is proved to be zero.

I have determined phosphorus twice in sample No. 4 filtering magnesium ammonium phosphate on asbestos felt in a Gooch crucible. These determinations are uncorrected for admixed silica and ferric oxide, and each gave 0.109 per cent. phosphorus.

#### WASHING MAGNESIUM AMMONIUM PHOSPHATE.

Sample number.	Percentage of phosphorus.	Magnesium chloride added. Gram.	Ammonium chloride present. Grams.	Ammonium chloride present per cc. Gram.	Volume of precipitation.	Volume of washing fluid.	Magnesia mixture used.	Washing fluid.
1	0.103	0.0432	6.00	0.100	60	250	1	7.25 per cent. ammonia.
1	0.103	0.0432	6.00	0.100	60	250	1	
3	0.096	0.0864	1.20	0.017	69	215	1	2.50 per cent. ammonia.
3	0.099	0.0864	1.20	0.017	69	215	1	
4 <sup>1</sup>	0.103	0.077	5.00	0.050	100	220	2	9.67 per cent. ammonia having dissolved in 100 cc. 2.50 grams of ammonium nitrate.
4 <sup>1</sup>	0.105	0.051	5.00	0.057	87	240	2	

<sup>1</sup> Blair's Chemical Analysis of Iron. First Edition, p. 82.

The varying figures for ammonium chloride and for magnesium chloride are without significance. Although the last two washing fluids show dissolving power on this precipitate, when used in excessive amount, they are satisfactory as customarily employed, as follows :

Number of the estimation.	Sample number.	Percentage of phosphorus.	Magnesium chlo-ride added. Gram.	Ammonium chlo-ride present. Grams.	Ammonium chlo-ride present per cc. Gram.	Volume of precipi-tation.	Volume of wash-ing fluid.	Percentage of am-monium in solu-tion of precipita-tion.	Magnesia mixture used.	Washing fluid.
	1	0.104	0.130	6.0	0.10	60	100	7.25	1	2.5 per cent. ammonia.
	1	0.101	0.130	6.0	0.10	60	100	7.25	1	
44	2	0.104	0.130	6.0	0.08	74	90	2.50	1	
45	2	0.102	0.130	6.0	0.09	67	90	2.50	1	
46	2	0.104	0.130	6.0	0.09	67	90	2.50	1	9.67 per cent. ammo-nia having dissolved in 100 cc. 2.5 grams of ammonium nitrate.
	1	0.103	0.086	6.0	0.10	60	100	7.25	1	
	1	0.103	0.086	6.0	0.10	60	100	7.25	1	
	2	0.103	0.086	6.0	0.11	53	100	7.25	1	
	2	0.101	0.086	6.0	0.10	60	100	7.25	1	
	2	0.103	0.086	6.0	0.09	67	100	7.25	1	

EXPERIMENTS IN ESTIMATING PHOSPHORUS IN SOLUTION OF SODIUM PHOSPHATE.

The solution was prepared from a salt purchased as chemically pure. This was recrystallized, filtered on the suction-pump, and washed once with cold water. The purified salt was dissolved in water and preserved in a ground glass-stoppered bottle, portions of it being filtered as used. Two quantities of twenty cc. each were evaporated to dryness and ignited in a weighed platinum capsule. The weights of phosphorus calculated from the two weights of sodium pyrophosphate obtained were 0.01008 and 0.01008. If these are expressed as percentages of phosphorus obtained by analysis of ten grams of steel, they would be 0.1008 and 0.1006. The following are the determinations of phosphorus in the solution, by precipitation as magnesium ammonium phosphate, using twenty cc. of the filtered solution for each precipitation.

No. 2 magnesium mixture was used in the determinations of the following table, and 7.25 per cent. ammonia for precipitation and washing fluid.

Number of the estimation										
1	2	cc of hydrochloric acid of 1.20 sp gr.	cc of magnesia mixture.	Molybdic acid Gram	Method of adding magnesia mixture.	Ammonia or magnesia mixture added last.	Volume for precipitation.	Volume of washing fluid.	Weight of magnesium pyrophosphate.	Phosphorus expressed as a percentage for ten grams of steel.
7	2	7	3	0.61 0.61	A A	X X	60 60	81 73	0.0365 0.0369	0.102 0.103



for the first three cc. added. After the first three cc. the remainder was dropped in continuously. The A additions occupied about one minute each, the B each about one-half hour or more.

In estimating phosphorus in steel by the molybdate-magnesia method, owing to the number of details involved, when separating molybdenum before the final precipitation as magnesium ammonium phosphate, it is difficult to decide whether its removal, in cases uncomplicated by the presence of arsenic, is advantageous or not. Estimations Nos. 1 to 7 inclusive give some light upon this point. Here there is no difference in results whatever, when precipitating with molybdic acid absent, and in presence of 0.61 gram of molybdic acid (approximately the weight present in analyzing steel of about 0.100 per cent. phosphorus, when employing ten grams in an analysis). There is no apparent difference in the results for Nos. 1, 2, 5, and 6, where three cc. of magnesia mixture were used in precipitating, and Nos. 3, 4, and 7, where ten cc. of magnesia mixture were used. This is because the precipitation had largely occurred before the larger excess of magnesium chloride entered the solution. These first seven are slightly too high. Because, although the magnesia mixture was added rather slowly, it was not added slowly enough to entirely eliminate plus error.

As in the first seven, so also in the remaining ones, the several determinations are duplicated, having no molybdic acid present in the solution when making one precipitation and 0.61 gram when making the other precipitation. The true result, as given by the sodium pyrophosphate determinations, being 0.1007, that is, approximately 0.101. Nos. 8 and 9 give this percentage, being results of almost ideal accuracy. The details differ from the first seven only in the rate at which magnesia mixture was dropped in. On the contrary, the rate of dropping in No. 10 was much increased, even over the first seven, and a greater plus error results, than in these.

In examples Nos. 11 to 14 inclusive the effect of decreasing the amount of ammonium chloride is illustrated. By contrasting Nos. 8 and 9 with Nos. 15 to 20 inclusive, the effect of reversing the order of addition of magnesia mixture and ammonia is seen.

		Percentage of phosphorus.	
No. 8.....		0.1011	
" 9.....		0.1011	
Mean .....		0.1011	
Sodium pyrophosphate determination		1	0.1008
"	"	2	0.1006
Mean .....		0.1007	
No. 15.....		0.0999	
" 16 .....		0.0994	
" 17 .....		0.1005	
" 18 .....		0.1002	
" 19 .....		0.0994	
" 20 .....		0.0991	
Mean .....		0.0998	

Nos. 21 and 22 show that even with the order of addition reversed, and with the extremely slow addition of magnesia mixture, the results are too high for large excess of precipitant, when the ammonium chloride is sufficiently reduced.

When magnesium chloride is added not in excess to solutions containing only a small quantity of free ammonia, or is thus added to those containing a large amount of free ammonia, some distinct quantity of phosphoric acid remains unprecipitated, as is well known. The same thing is true if an excess of magnesium chloride is added to a solution containing a large amount of free ammonia. Compare Nos. 8 and 9 with Nos. 15 to 20 inclusive. Filtrates from precipitations like Nos. 8 and 9 have, when examined for phosphoric acid, shown no trace, whereas in the class of precipitations represented by Nos. 15 to 20 inclusive a distinct reaction for phosphoric acid is obtained. This is not to be regarded as the solution of magnesium ammonium phosphate as such, but as the result of partial decomposition of this precipitate, at the moment of its formation by ammonia, with formation of ammonium phosphate and magnesia. The magnesia is dissolved by ammonium chloride if this is present in sufficient quantity, otherwise it remains to introduce plus error.

In large quantity of free ammonia then, the tendency to this reaction is more marked than in solutions containing only a small

quantity of free ammonia. Hence the reaction occurs only in nearly neutral solution when not reinforced by excess of magnesium chloride, whereas in solutions strongly ammoniacal, it occurs even if magnesium chloride is present in large excess. When magnesium chloride is added in excess too rapidly, or when the amount of ammonium chloride is much reduced, for either order of addition of ammonia and magnesium chloride some magnesia is precipitated. This occurs for too rapid addition, because as we may consider under this condition, a phosphate of magnesium is formed containing more magnesia than magnesium ammonium phosphate. It is conceivable that this may remain unchanged, giving too great weight after ignition, but I prefer to regard the reaction here, as being like that in the cases already considered. Thus the abnormal precipitate at the moment of its formation is partially decomposed by ammonia, and magnesium ammonium phosphate and magnesia are formed. If there is enough ammonium chloride present, and if the magnesium chloride is not added too fast, giving too rapid formation, the magnesia precipitated is redissolved as in cases already described. I do not regard the contamination by excess of magnesia mixture as mechanical.<sup>1</sup> The relative bulks of precipitates in Nos. 8 to 14 inclusive, a series carried out simultaneously, are against this idea, No. 14 being at least ten times the bulk of Nos. 8 or 9. Nos. 11 to 14 inclusive were the larger, and No. 14 the largest of the series. It is true that a bulky precipitate carries down more salt from solution than a crystalline one. In this regard the contamination is in part perhaps mechanical, but the bulk itself is not the chief cause, but an effect of contamination. Not only the size of such precipitates but their character show this.

<sup>1</sup> Gooch : *Am. Chem. J.*, 1, 391.

# THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF CHROMIUM, WITH SPECIAL REFERENCE TO THE ANALYSIS OF ROCKS AND ORES.<sup>1</sup>

BY W. F. HILLEBRAND.

Received April 14, 1898.

## INTRODUCTION.

HAVING occasion to analyze a number of highly titaniferous magnetites containing chromium, phosphorus, and vanadium, it became a serious problem to effect satisfactory separations of all these bodies in a form fit for separate determinations. The method of T. Fischer<sup>2</sup>—digestion of the precipitated lead salts with a strong solution of potassium carbonate—appears to offer the long-needed satisfactory quantitative separation of arsenic, phosphorus, chromium, tungsten, and molybdenum from vanadium, the normal lead meta-vanadate remaining quite unattacked, according to the author, while the other lead salts are wholly decomposed, but the applicability of this method to the separation of the minute amounts often found in rocks and ores has not been tested. The time required is considerable, hence it was desirable to devise a more rapid way for determining both chromium and vanadium without resorting to this separation. That this object has been measurably achieved, with certain limitations as to vanadium, the work thus far done seems to indicate. The present paper will deal only with the rapid estimation of chromium either in absence or presence of any or all of the elements above mentioned.

In view of the high coloring power of the chromates, it is surprising that this property does not seem to have been made the basis for a quantitative method for the estimation of chromium. A search through some of the more important textbooks has revealed no reference to such a method, and I am unaware that one has even been suggested. Yet the results attainable by colorimetric comparisons of dilute alkaline solutions of unknown strength with those of a known standard, leave little to be desired in point of quantitative accuracy.

As with colorimetric methods in general this one gives better results with small than with large percentages of chromium, yet it can be applied in the latter cases with very fairly satisfactory

<sup>1</sup> Read before the Washington Section, March 10, 1898.

<sup>2</sup> Inaugural Dissertation, Rostock, 1894.

results by making a larger number of consecutive comparisons with the same solution.

#### OUTLINE OF METHOD.

The chromium is brought into a measured volume of solution as monochromate rendered alkaline by sodium carbonate, and the whole or a portion of this solution is then compared with a definite amount of a somewhat stronger standard likewise made alkaline with sodium carbonate. The latter is diluted with water till both seem to be exactly alike in color, when a simple calculation gives the amount of chromium sought. The actual comparison takes little time and any number of repetitions can be made if desired in order to secure greater accuracy from the mean of a large number of observations. The preparation of the solution to be tested offers nothing novel, but certain precautions have to be observed therein as well as in the color comparisons which will be touched upon later.

#### TESTING OF METHOD BY COMPARISON OF STANDARD SOLUTIONS.

Two standard solutions were prepared by dissolving 0.25525 and 0.5105 gram potassium chromate in one liter of water made alkaline by a little sodium carbonate, each cubic centimeter then corresponding respectively to one-tenth and two-tenths milligram chromic oxide, in which latter form chromium is usually reported in rocks and ores. Definite amounts of one of the standards were then diluted with varying amounts of water in a tall, square glass vessel with exactly parallel sides. Into an exact duplicate of this vessel five or more cc. of the standard were introduced from a burette and diluted with water from another burette till exact agreement seemed to be reached on looking through the glasses horizontally.

In the following tables are recorded all observations without regard to the sequence in which they were made. No greater pains were taken to get exact agreement of color than are ordinarily observed in our routine titanium estimations, which are carried out in a precisely similar manner, so that the results may be taken to represent every-day work without extreme precautions. In only two cases can the observations be considered really bad, *viz.*, the third comparison of No. 6 and the first of No. 16.

TABLE I.

Ten cc. standard represent one milligram chromic oxide.

Test solution:		Comparison standard.							
No.	Standard. cc.	Diluted with water. cc.	cc.	H <sub>2</sub> O added. cc.	Contents as chromic oxide. Milligrams.	Chromic oxide found. Milligrams.	Chromic oxide present. Milligrams.	Error. Milligram.	Chromic oxide. Per cent. found.
1	10 <sup>1</sup>	90 <sup>1</sup>	5	44.00	0.5	0.98	1	—0.02	98.0
2	20 <sup>2</sup>	80 <sup>2</sup>	5	21.00	0.5	1.92	2	—0.08	96.0
3	40	60	10	14.60	1.0	4.06	4	+0.06	101.5
4	40	60	9.7	14.25	0.97	4.05	4	+0.05	101.2
			10	13.95	1.0	4.17	4	+0.17	104.4
			10	14.30	1.0	4.11	4	+0.11	102.9
			10	14.20	1.0	4.13	4	+0.13	103.3
5	40	60	10	14.65	1.0	4.05	4	+0.05	101.4
			10	15.65	1.0	3.90	4	—0.10	97.5
6	40	60	10	15.25	1.0	3.96	4	—0.04	99.0
			10	14.30	1.0	4.11	4	+0.11	102.9
			10	13.15	1.0	4.32	4	+0.32	108.0
			10	14.75	1.0	4.04	4	+0.04	101.0
			20	29.50	2.0	4.04	4	+0.04	101.0
7	50	50	10	9.75	1.0	5.06	5	+0.06	101.2
8	50	50	10	10.00	1.0	5.00	5	0.00	100.0
9	60	40	10	7.20	1.0	5.81	6	—0.19	96.7
10	75	25	20	6.65	2.0	7.505	7.5	+0.005	100.1
			20	6.60	2.0	7.519	7.5	+0.019	100.2
			10	3.15	1.0	7.605	7.5	+0.105	101.4
			15	4.70	1.5	7.610	7.5	+0.11	101.5
11	10	10	10	10.15	1.0	0.992	1	—0.008	99.2
			20	19.75	2.0	1.006	1	+0.006	100.6
12	10	11	10	10.60	1.0	1.02	1	+0.02	102.0
13	14.2	26.9	10	18.60	1.0	1.43	1.42	+0.01	100.7
			20	35.70	2.0	1.47	1.42	+0.05	103.5
14	15	24.35	10	16.55	1.0	1.48	1.5	—0.02	98.7
15	16	20	10	13.30	1.0	1.54	1.6	—0.06	96.2
			20	24.30	2.0	1.63	1.6	+0.03	101.9
16	31.9	20.6	10.5	8.10	1.05	2.96	3.19	—0.23	92.8
			20.5	14.20	2.05	3.10	3.19	—0.09	97.2
17	62.05	22.3	20	7.00	2.0	6.25	6.205	+0.45	100.7
			40	12.00	4.0	6.49	6.205	+0.285	104.6

Mean percentage found, 100.5.

<sup>1</sup> Color in this dilution too faint.<sup>2</sup> Limit of dilution for clear distinction of color in a thickness of three and three-tenths cm.

TABLE II.

Varying amounts of standard No. 2 (1 cc. = 0.2 mg.  $\text{Cr}_2\text{O}_3$ ) diluted till of the same concentration as standard No. 1.

No.	cc.	Standard.		Chromic oxide found per 100 cc. Milligrams.	Chromic oxide present in 100 cc. Milligrams.	Error. Milligram.	Chromic oxide. Per cent. found.
		Water added. cc.	Contents as chromic oxide. Milligrams.				
18	5	5.2	1	9.80	10	-0.2	98.0
19	10	9.95	2	10.02	10	+0.02	100.2
20	15	15.8	3	9.74	10	-0.26	97.4
21	20	20.0	4	10.00	10	0.00	100.0
22	30	29.5	5	10.08	10	+0.08	100.8
Mean 99.3		Grand mean 100.36.					

The first table and the grand mean show an apparent personal tendency toward slightly high results, though it is possible that this is due to a slight difference in the internal dimensions of the two glasses, the same one always having been used for the standard solution. If this is so, a long series of tests with glasses reversed should give a general mean slightly below 100.

#### TESTING THE METHOD ON ORES AND ROCKS.

In order to prove the value of the method in rock analysis, varying amounts of the standard solution were evaporated in a large crucible with five grams of an iron ore carrying phosphorus and vanadium, and fused with twenty grams of sodium carbonate and three grams sodium nitrate. The aqueous extract, after reduction of manganese by methyl or ethyl alcohol, was nearly neutralized by nitric acid and evaporated to secure approximate separation of silica and alumina. As a precautionary measure, since a little chromium is usually carried down, the precipitate was ignited, silica was removed by hydrofluoric and sulphuric acids, the residue was fused with sodium carbonate, and alumina again separated as before. To the combined filtrate was added mercurous nitrate and the slightly washed copious precipitate of phosphate, chromate, vanadate and carbonate of mercury was ignited with the paper in a platinum crucible, which can be done without much fear of loss or of injury to the crucible. The residue was then fused with a little sodium carbonate, extracted with

water, filtered into a graduated flask and made up to 50 or 100 cc., according to the intensity of the color, and compared with the standard. A similar operation was carried out with a silicate rock. Table III shows the results.

TABLE III.

No.	Chromic oxide added. Milligrams.	Chromic oxide found. Milligrams.
I. Five grams iron ore.....	7.03	7.18
	...	7.20
	...	7.25
	...	7.21
II. Five grams iron ore.....	2.99	3.08
	...	3.13
III. Two grams silicate.....	1.6	1.53
	...	1.57
	...	1.59

When the percentage of chromic oxide in an ore or mineral is more than about two-tenths per cent. and vanadium has not also to be estimated, much time may be spared by at once taking the color of the original extract from the sodium carbonate fusion, after insuring complete reduction and removal of manganese, and perhaps concentrating: But if the chromium is much less than this amount, and especially if several grams of powder have been operated on, it becomes difficult or impossible to obtain a filtrate of sufficiently small bulk to show a decided color. Therefore, in such cases, and when vanadium is likewise to be estimated, it is necessary to precipitate as above with mercurous nitrate in order to eventually have a small bulk of sufficiently colored solution. Even then, for very minute amounts, it is necessary to use Nessler tubes exactly as in ammonia estimations.

If niter has been used in the fusion and the crucible has been attacked by it, a yellow color of the filtrate may be due to dissolved platinum, but neither the proportion of niter nor the temperature of the blast should ever be high enough to permit the crucible to be attacked.

#### THE COLORIMETRIC APPARATUS AND ITS USE.

The glasses employed were of approximately square section, about twelve cm. high and three and three-tenths cm. inside meas-



urement, with exactly parallel sides, and of course as nearly alike as they could be obtained. One pair of opposite sides of each should be blackened. With glasses of the thickness mentioned it is generally advisable to use from five to ten cc. of standard at a time and to so regulate the strength of the solution to be tested that it shall contain more than two milligrams chromic oxide in 100 cc. which is about the limit of distinct visibility in a thickness of three and three-tenths cm.

In order to exclude the effect of side light in this and other similar methods (titanium for instance), it is very convenient to have a simple light box that can be easily held in one hand, about thirty-five cm. long and thirteen to fourteen cm. square, painted black inside and out and with one end closed by a piece of ground glass, the other open. For a space equal to the width of the glasses the cover is removed at the top next the glass end, to permit of the insertion of the glasses, side by side, in such a way that no light shall penetrate around their sides or between them. A stiffly sliding, black, cardboard shutter is movable up and down immediately back of the glasses, so that all light can be cut off except that which comes through the liquid.

Precautions of this kind are necessary if accurate results are to be counted on. Except for mere traces this simple combination of glasses and darkened box ensures greater accuracy and rapidity of work than Nessler tubes and is preferable likewise, so far as my own experience goes, to expensive instruments like the colorimeter of Soleil-Duboscq, etc. The glasses should, of course, have exactly parallel sides and equal diameters, though they may perhaps be made with advantage rather narrow in one direction to permit of using smaller bulks of liquid.

In making the color comparisons the box is best held close to a window, so as to get a full strong light. The condition of the light seems to make an appreciable difference in the accuracy of the comparisons, all of which were made by daylight.

#### ACCURACY OF RESULTS.

Especially for comparatively and very small amounts of chromium the method gives exact results, better than can ordinarily be hoped for from any gravimetric method, considering

the fact that as a rule other substances are present which it is extremely difficult to remove completely.

A few comparisons between colorimetric and gravimetric determinations of chromium in a few rocks are here given to show the order of agreement, the former having been made several months and even years after the latter.

Gravimetric. Per cent.	Colorimetric. Per cent.
trace	0.018
0.05	0.051
0.14	0.12
0.08	0.083
trace	0.013
none	0.0086
none	0.0067

The outcome was somewhat of a surprise, for it was scarcely to be expected that the long and laborious gravimetric separations should have resulted so well as they are shown to have done. It should be mentioned that for the gravimetric tests but one or two grams at most were used, which accounts for the reported absence of chromium in two instances, this report being based on the lack of color in the aqueous extract of the alkaline fusion after removal of manganese.

No experiments have been made with high percentages, but the tables give with certainty the degree of accuracy even then attainable. Whether the chromic oxide to be estimated is one-tenth per cent. or one hundred per cent., the percentage result is the same provided the dilution is alike in each case. For instance, if 99.5 per cent. is found in a total solution of 100 cc. containing 0.01 gram chromic oxide, the same percentage holds if the total volume were ten liters holding one gram chromic oxide.

It is probably inadvisable to increase the strength of the standard much above that of No. 2 above, containing two-tenths milligram chromic oxide in form of potassium chromate to the cubic centimeter.

No tests have been made with other alkaline solutions than sodium carbonate, in order to ascertain if there is a difference in the color intensities for like dilution, nor is it probably important to do so.

**VOLUMETRIC ESTIMATION OF VANADIUM IN PRESENCE  
OF SMALL AMOUNTS OF CHROMIUM, WITH SPE-  
CIAL REFERENCE TO THE ANALYSIS OF  
ROCKS AND ORES.<sup>1</sup>**

**BY W. F. HILLEBRAND.**

Received April 14, 1898.

**OUTLINE AND LIMITATIONS OF THE METHOD.**

**W**HEN chromium and vanadium occur together and the former has been estimated colorimetrically as detailed in the preceding paper,<sup>2</sup> the vanadium can in many instances be

presence of molybdenum, and arsenic must first be removed by hydrogen sulphide if present.

#### TESTING THE METHOD.

A solution of sodium vanadate was prepared by fusing 0.937 gram of pure vanadium pentoxide with sodium carbonate and diluting to one liter. Each cubic centimeter contained 0.000937 gram vanadium pentoxide. Of this, sufficient amounts were mixed with varying volumes of a standard solution of potassium chromate. After in some cases determining chromium colorimetrically, sulphuric acid was added, sulphur dioxide gas<sup>1</sup> introduced for a few moments, and the excess of the latter expelled by boiling in a rapid current of carbon dioxide, without which its complete expulsion is difficult. When cooled to from 70°–80° C. the titration was made with very dilute solution of permanganate corresponding to about one milligram vanadium pentoxide to the cubic centimeter as calculated from its equivalent in iron. By repeating the reduction and boiling, any number of check-tests can be rapidly made in the same solution. The solutions ranged in bulk from 50 to 200 cc. according to the amounts of chromium added.

With the larger chromium contents the differences in the quantity of permanganate used, according as titration was effected at practically boiling temperature or a somewhat reduced one, were very apparent. In one case at nearly boiling heat, ten milligrams of chromic oxide were largely oxidized to chromium trioxide, as shown by the change of color from dark green to yellow. Even at 70°–80° with this amount of chromium the results for vanadium will be too high unless the precaution is taken to ascertain the needed correction by adding permanganate to an equal bulk of hot chromic sulphate solution containing approximately the same amount of chromium. When this is done, however, the results are satisfactory even when as much as thirty milligrams of chromic oxide are present and only one or two milligrams of vanadium pentoxide.

<sup>1</sup> The direct use of a solution of sulphur dioxide or of an alkaline sulphite is inadmissible unless these have been freshly prepared, since after a lapse of time they contain other oxidizable bodies than sulphurous acid or a sulphite. The sulphur dioxide is best obtained as wanted by heating a flask containing a solution of sulphur dioxide, or of a sulphite to which sulphuric acid has been added.

Doubtless the modified iodometric method of 'T. Fischer' will in general give sharper results where chromium is present in considerable amount, and if so it should be preferred to titration by permanganate. But its use involves the preparation of a standard thiosulphate instead of the ever-ready permanganate solution, and the manipulations are more time-consuming. The object has been in the present case to reach satisfactory results with the greatest expedition, and when chromium is not present in considerable amount this is accomplished.

The following tables contain the results of a considerable number of tests, those in Table II being tabulated separately in order to show the degree of accuracy attainable with a large excess of chromium by applying the correction above mentioned and also the amount of this correction.

TABLE I.

No.	Chromic oxide Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Milligrams.	Error. Milligram.
1	1	9.37	9.22	-0.15
2	1	0.94	1.04	+0.10
			0.98	+0.04
3	1.5	5.25	5.49	+0.24
			5.43	+0.19
4	2	5.62	5.5	-0.12
			5.5	-0.12
5	3	4.68	4.78	+0.10
			4.78	+0.10
			4.83	+0.15
6	3	5.62	5.58	-0.04
			5.58	-0.04
7	3.5	18.74	18.89	+0.15
			18.97	+0.23
8	6	5.6	6.1	+0.50
9	6	4.68	4.78	+0.10
10	6	5.62	5.58	-0.04
11	10	5.62	5.58	-0.04
12	10	23.52	23.81	+0.29
			23.71	+0.19
13	10	46.86	46.68	-0.18

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# ESTIMATION OF VANADIUM.

again nearly neutralized, etc. To the combined alkaline filtrates was added mercurous nitrate, the phosphate, vanadate, chromate, and carbonate with platinum, fused with a little sodium carbonate, in water, and filtered into a small graduated flask. In the metric determination of the chromium, sulphuric acid, both chromium and vanadium were reduced by sulphur gas, and the titration carried out as described.

TABLE III.

No.	Chromic oxide. Milligrams.	Vanadium pentoxide. Milligrams.	Vanadium pentoxide found. Milligrams.
22 (Five grams iron ore)	7	6.76	6.81 6.48 6.43 6.37
23 (Five grams iron ore)	3	3	3.08 3.13 3.03 3.08
24 (Two grams silicate)	1.6	1.87	1.86 1.97 2.07 1.86

These and other experiments show that by taking five grams of ore or rock, vanadium, if present to 0.01 or 0.02 per cent., can be readily estimated by reasonable care in all the operations. Absolute confirmation of its presence can be easily obtained by evaporating the solution to remove excess of sulphuric acid, taking a few drops of dilute nitric acid, and adding to the test-tube a drop or two of hydrogen peroxide. In this way a positive or negative assurance as to the presence of vanadium is given when the result of titration alone might be doubtful. Addition of ether at the same time affords a simultaneous test for chromium by its blue color, and this might perhaps be of use, if necessary, to remove all, or the greater part of the chromium from the titration of the vanadium, since the titration product of the latter does not dissolve in the ether.

It is even possible that the dark brown color produced by hydrogen peroxide might be utilized for an exact method for estimating vanadium.

## NOTES.

*The Liquefaction of Hydrogen and Helium.*—A recent issue of the London *Times* states that Professor Dewar has liquefied both these gases at the Royal Institution. Hydrogen was produced to the amount of half a wineglassful in five minutes. The specific gravity of the liquid is stated as 0.6. The boiling-point of helium appears to be not very far from that of hydrogen.

*The International Congress of Applied Chemistry.*—The Organizations Committee of the Third International Congress of Applied Chemistry, to be held at Vienna, beginning July 28, begs to inform American chemists who propose to take part in that Congress, that a committee has been formed for the purpose of securing agreeable and cheap dwelling places for foreign members during the continuance of the Congress. Those wishing to engage such places should address: Wohnungscomite des III internationalen Congresses für angewandte Chemie, Wien IV/2 Schönburgstrasse 6.

The Organizations Committee also begs to inform American chemists that, on account of the Jubilee Exposition to be held in Vienna from the 7th of May to the 8th of October, this year, the Austrian railroads are prepared to furnish round-trip tickets to all points in Austro-Hungary at greatly reduced prices. A further communication from the Railroad Committee of the Third International Congress will be made to American chemists in a short time concerning this important matter.

I am also requested by Prof. Strohmer, the General Secretary of the Third International Congress of Applied Chemistry, to inform American chemists that the North German Lloyd Steamship Company has made the following reductions in fares to members to the Congress desiring to use its steamships during the coming summer.

Rates of fares are fixed for two seasons; *viz*: From the first of April to the first of November, called the summer season, and from the first of November to the 31st of March, called the winter season. The reduced rates for the two seasons are as follows:



# BOOKS RECEIVED.

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	Summer season.	Winter season.
For Steamships Kaiser Wilhelm der Grosse and Kaiser Friedrich.....	\$105.00	\$77.50
All other express steamers except those mentioned above.....	100.00	77.50
For Steamships Barbarossa, Friedrich der Grosse, Königin Luise and Bremen.....	80.00	65.00
All other mail steamers except those men- tioned .....	75.00	60.00

Arrangements should be made with the local representatives of the company, or with the New York agents, to secure the proper reduction. The presentation of the membership card will be sufficient evidence of the right of the applicant to secure the reduced rates.

No information has been sent in regard to further reductions for round-trip tickets. Arrangements, if any, for these reductions should be made with the agents of the company. The prices given above are for the best rooms of the first class, and the Steamship Company will accord to members of the Congress the best quarters if application be made in time.

H. W. WILEY,  
*Chairman American Committee.*

## ERRATUM.

*The Volatility of Titanic Oxide.*—Mr. W. F. Hillebrand, Washington, D. C., has called attention to an erroneous statement in the paper on "The Commercial Analysis of Bauxite."<sup>1</sup> It is that titanic oxide is volatile under the action of a mixture of sulphuric and hydrofluoric acids. This is a mistake. There is a very trifling loss of titanic oxide when a mixture of these two acids is employed, and it arose from a misinterpretation of some notes, for which Mr. Hancock is in no wise responsible. I am obliged to Mr. Hillebrand for drawing attention to this error.

WM. B. PHILLIPS.

## BOOKS RECEIVED.

1. Variation in the Amount of Free and Albuminoid Ammonia in Waters on Keeping. 2. Corrosion of Aluminum. 3. Crystallized Carbon Dioxide. 4. On the Internal Structure of Gold Nuggets. 5. Contribu-

<sup>1</sup> This Journal, 20, 209.

tions to the Bibliography of Gold. By A. Liversidge, Professor of Chemistry, University of Sidney, N. S. Wales. 22 pp.

Methods for the Analysis of Ores, Pig Iron, and Steel in use at the Laboratories of Iron and Steel Works in the Region about Pittsburgh, Pa., together with an Appendix Containing Various Special Methods for Analysis of Ores and Furnace Products. Contributed by the Chemists in Charge, and Edited by a Committee of the Chemical Section, Engineers' Society of Western Pennsylvania. Easton, Pa.: The Chemical Publishing Co. 1898. v + 133 pp. Price: cloth, \$1.00; paper, 75 cents.

Animal Fats and Oils. By Louis Edgar And  s. Translated by Charles Salter. 62 illustrations. xii + 240 pp. 1898. New York: D. Van Nostrand Co. Price, \$4.00.

The John Crerar Library. Third Annual Report for the Year 1897.

Preparation and Application of Fungicides. Bulletin 125, Connecticut Agricultural Experiment Station, New Haven, Conn.

The Truth about Cigarettes. Papers read and discussed by The Medico-Legal Society. 48 pp. Price, 10 cents.

Bulletin No. 43. I. Soils. II. Climate. III. Water Supply. IV. Irrigation Equipment. Report from Beeville Station. April, 1897. 30 pp. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas.

Bulletin No. 44. Paints and Painting Materials and Miscellaneous Analyses. July, 1897. 15 pp. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas.

Administrative Report of the State Geologist from October 24, 1894, to October 15, 1896, inclusive. 45 pp. and five half-tone plates. Administrative Report of the State Geologist for the Year Ending October 15, 1897. 20 pp. and three half-tone plates. W. S. Yeates, State Geologist. Geological Survey of Georgia, Atlanta, Georgia.

A Preliminary Report on the Marbles of Georgia. By S. W. McCallie, Assistant Geologist. Bulletin No. 1, 1894. 92 pp., with numerous half-tones and maps. 1894. Geological Survey of Georgia, Atlanta, Ga.

A Preliminary Report on the Corundum Deposits of Georgia. By Francis P. King, Assistant Geologist. 138 pp., with half-tones and maps. 1894. Geological Survey of Georgia, Atlanta, Ga.

A Preliminary Report on a Part of the Water-Powers of Georgia. Compiled from the notes of C. C. Anderson, Late Assistant Geologist, and from other sources. By B. M. Hall, Special Assistant. 1896. 153 pp., with half-tones and maps. Geological Survey of Georgia, Atlanta, Ga.

A Preliminary Report on a Part of the Phosphates and Marls of Georgia. By S. W. McCallie, Assistant Geologist. 103 pp., with half-tones. 1896. Geological Survey of Georgia, Atlanta, Ga.

Constitution of the New England Association of Chemistry Teachers, adopted February 19, 1898, Lyman C. Newell, President, and Irving O. Palmer, Newtonville, Mass., Secretary.

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

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### EVAPORATION AND PLANT-TRANSPIRATION.

BY WALTER MAXWELL.

Received April 12, 1898.

THE data which largely compose this contribution were obtained in the course of observations bearing upon the factors which enter into a system of rational and economic irrigation, and in connection with the study of certain practical questions that relate to land irrigation on the Hawaiian Islands. These data, however, have also a more purely scientific value, and may have an interest for those who are more exclusively engaged in physiological investigations.

The actual purpose of the observations which these data represent was to try to determine : first, the loss of moisture due to direct evaporation from the soil ; and secondly, the relative proportion that escapes by transpiration from the sugar-cane (*saccharum officinarum*) during different periods of growth, and to note the meteorological and other factors which appear to control these phenomena.

The observations on soil-evaporation and plant-transpiration were made as follows : A given weight of the particular soil was put into two tubs, exactly 125 pounds into each tub. The tubs had perforated bottoms, over which a piece of linen cloth was laid before putting in the soil, in order to prevent the soil dropping through, or blocking up the holes. When filled thus with soil, the tubs were each set into a galvanized iron pan containing water, the water being kept up to a given mark or level,

which level was the point of contact between the soil in the tubs and the water in the pans. The pans were most carefully covered with moisture-proof glazed oilcloth, to prevent any evaporation from the pans except through the tubs containing the soil. When the tubs were set in place, water was added to each pan by means of a funnel that was inserted through the waterproof covers, and in sufficient volume to saturate the soil, whose absorptive power was 48.2 per cent. on its own weight. This was done on April 15, and on April 16 three pieces of seed-cane were planted in tub No. 2, whilst in tub No. 1 no cane was planted, the latter having to record the escape of water by means of the soil, and No. 2 tub the loss by means of the soil plus the growing cane.

The tubs were placed upon a veranda, having a south exposure and a strong light, but as they had to be protected against rainfall they were so located that no direct sunlight fell upon them. Near by the tubs, temperature readings were taken. The maximum and minimum thermometers gave the extremes of temperatures, and the dry-bulb and wet-bulb thermometers the indications of "humidity in the air."

It has commonly been claimed that temperature and the "relative humidity in the air" are controlling factors in evaporation. The writer, however, has believed not only that there is not necessarily a constant relation between temperature, atmospheric moisture, and the water given off from soil and water surfaces, but that there are other factors whose individual action exceeds the united influences of the factors already stated. For this reason we decided, at the time of taking the temperature and humidity readings, to determine the actual evaporation, by use of evaporators. The form of evaporator used was a small galvanized dish, one inch deep, and having a superficial area of 120 square inches. The evaporator was placed between the dry- and wet-bulb thermometers, thus having the same protection against the sun and exposure to the wind. At seven o'clock in the morning 500 grams of water were weighed into the evaporator, and at the end of twenty-four hours the weight was retaken and recorded. The water was made up again in weight to 500 grams, proceeding thus daily over the whole period of time included by the experiment. In addition to the evaporator

described, a second one, in each item exactly identical with the former, was used. This second one was placed in a barn. The large doors of the barn were kept open day and night, thus providing an ample circulation of the outer air, but no violent wind disturbance or sudden movements of the air. The purpose in this case was to have the corresponding conditions of temperature and atmospheric humidity surrounding the former evaporator located thirty feet distant, with the exclusion of the factor of wind. The data furnished by the two evaporators were taken and recorded in the same way, with the corresponding thermometer readings. With this brief description of the mode of observation, the data are now given. These are numerous and occupy considerable space, but the full statement is necessary in order to observe the wide range of variations. Two statements could be made with some advantage, from the data. The soil-evaporation and the transpiration by the cane, however, are so bound up with the meteorological conditions that we present it as a whole :

Date, 1897.	Mean outdoor evaporation.	Outdoor evaporation.	Mean indoor temperature.	Indoor evaporation.	Humidity.	Direction of wind.	Evaporation of soil No. I. Saturated. cc.	Evaporation of soil and cane No. II. Cane planted. Saturated. cc.
April 16	74	27.6	78	10.4	76.3		....	....
" 17	76	27.6	79	10.6	73.8		1000	1000
" 18	75	32.0	80	13.2	90.4		800	800
" 19	76	34.0	80	13.0	73.8		1000	1000
" 20	76	37.6	79	14.4	76.3		500	500
" 21	76	36.6	79	13.4	76.4		200	200
" 22	75	31.4	80	14.0	76.4		500	500
" 23	75	32.0	79	12.2	73.8		700	700
" 24	74	33.4	77	13.0	73.7		700	700
" 25	72	27.2	76	10.6	78.9		500	500
" 26	75	30.2	78	11.2	76.3		700	700
" 27	75	27.0	76	11.2	78.9		500	500
" 28	76	32.2	78	13.6	76.3		500	500
" 29	74	20.2	70	12.6	76.3		700	700

Date, 1897.		Mean outdoor evaporation.	Outdoor evaporation.	Mean indoor temperature.	Indoor evaporation.	Humidity.	Direction of wind.	Evaporation of soil No. I.	Evaporation of soil and cane No. II.
								Saturated. cc.	Cane planted. Saturated. cc.
May	3	72	34.2	77	11.8	78.9		500	500
"	4	75	38.2	79	12.6	73.7		500	500
"	5	75	29.2	79	11.4	78.9		500	500
"	6	77	35.4	79	13.2	76.4		500	500
"	7	75	34.4	81	13.4	71.5		500	500
"	8	71	19.2	78	6.8	78.9		500	500
"	9	72	17.2	79	11.0	76.4		500	500 <sup>1</sup>
"	10	73	25.6	80	10.0	81.8		300	300
"	11	75	27.2	83	12.6	79.1		300	300
"	12	73	22.2	79	10.6	76.4		300	300
"	13	75	25.8	80	12.2	71.5		300	300
"	14	76	22.2	80	10.8	79.0		300	300
"	15	74	23.0	77	9.0	84.5		300	300
"	16	73	11.0	78	4.2	87.4		300	320
"	17	73	11.0	78	6.0	84.6	S. E.	300	330
"	18	77	25.2	81	11.0	79.1	N. E.	300	350
"	19	77	32.8	80	12.6	79.1	"	180	200
"	20	77	31.3	82	13.2	76.6	"	220	250
"	21	75	33.6	80	13.0	76.5	"	180	200
"	22	75	29.0	79	10.6	93.5	"	220	250
"	23	75	30.6	78	11.6	78.9	"	300	310
"	24	76	26.2	81	12.0	76.5	"	300	310
"	25	76	27.0	80	11.6	79.1	"	340	350
"	26	73	27.2	80	12.2	76.7	"	350	360
"	27	71	15.6	79	9.6	81.8	S. E.	450	500
"	28	76	30.0	81	12.6	76.6	E.	500	550
"	29	79	31.6	80	12.6	79.1	S. E.	500	550
"	30	78	35.2	82	14.0	79.1	E.	300	310
"	31	78	36.2	82	14.2	76.6	"	300	410
June	1	78	34.6	83	14.6	76.6	"	400	450
"	2	78	30.2	82	12.0	87.6	S. E.	350	400
"	3	78	24.0	81	11.0	79.1	"	450	500
"	4	76	30.0	81	13.2	76.5	N. E.	550	600
"	5	75	21.0	79	9.2	81.8	S. E.	450	500
"	6	75	24.8	80	10.6	81.8	"	400	500
"	7	75	24.0	79	9.6	79.1	N. E.	400	500
"	8	76	24.6	80	10.0	81.9	"	400	500
"	9	77	26.2	80	10.8	79.1	"	400	500

<sup>1</sup> The cane began to come up and twelve stalks were up by May 21.

Date, 1897.		Mean outdoor evaporation.	Outdoor evap- oration.	Mean indoor temperature.	Indoor evapo- ration.	Humidity.	Direction of wind.	Evaporation of soil No. I.	Evaporation of soil and cane No. II.
								Saturated. cc.	Saturated. Cane planted, cc.
June	10	77	28.6	81	12.0	79.1	N. E.	400	500
"	11	76	23.0	80	9.2	79.1	"	450	500
"	12	77	27.6	79	10.0	81.8	"	400	500
"	13	77	36.6	82	14.0	76.6	"	400	500
"	14	76	27.2	81	11.2	81.8	"	400	550
"	15	78	29.0	80	11.0	81.8	S. E.	400	550
"	16	79	31.0	82	12.0	81.9	"	400	500
"	17	78	28.2	83	12.0	81.9	N. E.	450	550
"	18	78	30.0	83	12.2	79.2	"	400	550
"	19	78	26.0	81	12.2	81.9	"	400	550
"	20	76	22.2	82	10.6	81.9	"	400	500
"	21	76	16.2	81	8.2	84.7	S. E.	400	500
"	22	74	12.6	80	9.2	84.6	S.	400	500
"	23	75	9.2	79	6.0	87.5	"	400	500
"	24	73	6.0	78	4.2	96.7	S. W.	200	400
"	25	77	13.4	81	9.6	87.6	S. E.	100	300
"	26	75	5.6	78	■.■	93.5	S.	100	300
"	27	76	13.4	82	9.6	84.7	"	100	300
"	28	76	13.0	83	9.0	82.0	S. W.	100	400
"	29	74	13.0	81	8.0	84.7	"	200	400
"	30	80	31.0	83	10.0	79.3	S. E.	200	500
July	1	78	26.0	84	12.0	76.7	E.	200	500

Date, 1897.		Mean outdoor evaporation.	Outdoor evap- oration.	Mean indoor temperature.	Indoor evapo- ration.	Humidity.	Direction of wind.	Evaporation of soil No. I.	Evaporation of soil and cane No. II.
								Saturated. cc.	Saturated. cc.
July	19	78	23.0	81	10.6	81.9	E.	400	700
"	20	76	23.0	81	10.0	81.9	N. E.	400	700
"	21	79	27.6	83	13.0	74.1	E.	400	700
"	22	78	25.4	82	12.0	74.0	"	400	700
"	23	79	29.0	82	12.0	76.6	"	400	700
"	24	79	29.0	84	14.0	71.7	"	400	700
"	25	79	20.6	84	11.2	71.7	"	400	700
"	26	80	28.0	83	12.2	74.2	"	400	700
"	27	79	28.8	83	13.2	74.1	"	400	700
"	28	79	32.2	84	15.2	76.7	"	400	800
"	29	78	25.2	83	12.0	76.7	"	400	800
"	30	77	26.0	84	12.8	76.7	E. S. E.	400	800
"	31	78	31.0	84	14.0	76.7	E.	400	800
Aug.	1	77	24.2	84	12.0	76.7	"	400	800
"	2	76	17.6	83	11.6	79.1	S. E.	400	800
"	3	79	18.2	85	11.0	76.7	"	400	800
"	4	80	23.0	86	12.0	76.8	E.	400	800
"	5	78	23.6	83	11.2	79.2	"	400	800
"	6	78	32.6	83	13.8	76.7	"	300	700
"	7	77	31.0	81	12.2	81.8	"	400	700
"	8	78	30.2	81	12.6	76.5	N. E.	400	800
"	9	79	31.6	84	14.0	71.7	"	400	800
"	10	79	26.2	84	13.0	71.7	E.	400	800
"	11	78	27.2	83	12.2	71.7	"	400	800
"	12	79	23.0	83	10.8	79.1	"	400	800
"	13	80	15.0	83	7.6	84.8	"	400	800
"	14	80	25.4	84	11.2	82.1	"	400	800
"	15	79	26.6	82	12.2	71.6	"	400	800
"	16	77	31.2	83	13.4	71.7	"	400	800
"	17	78	26.2	81	12.0	74.0	"	400	800
"	18	79	32.2	84	12.4	71.7	"	400	800
"	19	80	33.0	83	13.2	74.1	"	400	900
"	20	79	26.0	83	13.2	71.6	"	400	900
"	21	78	26.0	81	13.0	74.0	"	400	1000
"	22	78	26.0	82	12.0	74.0	"	400	1000
"	23	81	33.4	84	15.8	69.3	"	400	1000
"	24	80	29.6	84	14.4	74.2	N. E.	400	1000

! One stalk of cane died.



Humidity.	Direction of wind.	Evaporation of soil No. I.	Evaporation of soil and cane No. II.
		Saturated. cc.	Saturated. cc.
74.1	E.	400	1000
76.6	"	400	1000
74.2	"	400	1000
76.7	"	400	1000
71.7	"	400	1000
71.6	"	400	1100
57.0	"	400	1100
4.0	N. E.	400	1200
4.6	"	400	1200
1.3	"	400	1200
.0	"	400	1200
6	"	400	1200
1	"	400	1200
;	"	400	1100
	"	400	1100
	"	400	1000
	"	400	1000
	E.	400	1000
	N. E.	400	1000
	"	400	1000
	"	400	1000
	"	400	1000
	"	400	1000
	v. N. E.	400	1000
	S.	400	1000
	. v. W.	400	1000
	N. E.	300	800
	"	300	800
	"	300	800
	"	300	800

ned later, nitrogen  
application being  
water in the pan,  
of this application  
he cane, whereby  
on in tub No. 1

Date, 1897.	Mean outdoor evaporation.	Outdoor evaporation.	Mean indoor temperature.	Indoor evaporation.	Humidity.	Direction of wind.	Evaporation of soil No. I.	Evaporation of soil and cane No. II.
							Saturated.	Cane planted. Saturated.
							cc.	cc.
Sept. 24	78	32.2	81	11.2	74.0	N. E.	300	800
" 25	77	34.2	81	12.0	73.9	"	300	900
" 26	78	29.2	82	11.4	74.0	"	300	900
" 27	76	22.6	81	10.0	79.1	"	300	1000
" 28	80	26.6	82	11.2	79.2	S. v. N. E.	300	1200
" 29	80	34.2	82	12.6	76.6	"	300	1500
" 30	78	31.6	82	12.0	76.6	N. E.	300	1400
Oct. 1	78	32.6	81	11.0	76.6	"	300	1200
" 2	74	30.2	81	11.6	76.6	"	300	1200
" 3	76	23.6	82	11.0	74.1	"	300	1200
" 4	75	14.6	80	8.2	76.5	S. v. E.	300	1000
" 5	76	14.0	80	9.0	81.8	S.	300	1000
" 6	74	15.8	80	8.0	79.1	"	300	1000
" 7	79	25.2	81	10.2	76.6	S. v. N. E.	300	1000
" 8	79	24.0	84	10.2	74.3	N. E.	300	1000
" 9	78	14.0	83	8.0	82.1	"	300	1000
" 10	76	13.0	81	8.2	79.1	S.	300	1000 <sup>1</sup>
" 11	77	11.0	81	4.2	81.9	"	300	1000
" 12	77	25.2	79	9.0	81.9	S. v. N. E.	300	1000
" 13	78	31.2	80	11.2	79.1	N. E.	300	1000
" 14	77	29.8	81	13.0	79.1	"	300	1000
" 15	75	32.6	79	11.4	76.5	"	300	950 <sup>2</sup>
" 16	75	25.6	79	10.0	76.5	"	300	950
" 17	76	19.6	79	8.2	76.5	"	300	950
" 18	76	22.2	79	9.0	79.0	"	300	1000
" 19	76	16.6	80	8.6	79.1	"	300	1000
" 20	79	27.0	80	10.0	79.1	"	350	1000
" 21	79	31.0	80	10.4	79.1	"	350	1000
" 22	78	35.6	80	12.0	74.0	"	350	1100
" 23	75	20.0	80	7.6	81.9	"	350	1200
" 24	76	10.6	79	6.6	87.5	S.	400	1200
" 25	75	8.4	79	5.6	87.5	"	350	1000
" 26	76	9.6	80	6.6	87.6	N. W. v. S.	350	1000
" 27	75	8.6	80	6.6	87.5	S.	300	900
" 28	76	15.6	79	7.0	84.6	S. v. N. E.	300	800
" 29	76	17.0	79	8.0	81.8	N. E.	300	700
" 30	78	26.0	80	10.2	76.5	"	300	600

<sup>1</sup> Second stalk of cane died.

<sup>2</sup> Third stalk of cane died.

At this date a second application of 100 grams of sodium nitrate was made, it being observed that the vitality of the growing cane was decreasing, which was indicated by its yellowish appearance and by a falling off in transpiration. The evaporation from the soil in tub No. 1 still remained the same.

Date, 1897.	Mean outdoor evaporation.	Outdoor evaporation.	Mean indoor temperature.	Indoor evaporation.	Humidity.	Direction of wind.	Evaporation of soil No. I.	Evaporation of soil and cane No. II.
							Saturated.	Cane planted. Saturated.
							cc.	cc.
Oct. 31	75	24.8	81	10.0	76.5	N. E.	300	700
Nov. 1	77	29.6	79	11.0	76.4	"	300	900
" 2	72	30.0	78	10.0	78.9	"	300	1000
" 3	68	32.4	74	9.0	81.6	"	300	1000
" 4	76	31.0	78	10.6	78.9	"	300	1000
" 5	77	32.0	79	10.0	76.5	"	300	1100
" 6	78	37.0	79	12.0	76.4	E.	300	1100
" 7	78	38.0	81	11.6	74.0	N. E.	300	1100
" 8	77	41.2	78	12.4	78.9	"	300	1100
" 9	76	41.0	79	12.6	76.4	"	300	1100
" 10	74	25.0	79	10.0	76.4	"	300	1100
" 11	73	16.0	77	7.4	78.9	W. v. S.	300	1200
" 12	72	15.6	78	8.6	81.7	S.	300	1100
" 13	72	14.2	77	8.0	84.5	"	300	1000
" 14	73	14.0	77	8.0	84.5	S. v. E.	300	1000
" 15	72	12.2	77	6.2	84.6	"	300	1000
" 16	72	12.6	76	7.2	81.6	S.	300	1000
" 17	74	13.0	78	8.0	87.5	"	300	1000
" 18	73	8.0	77	5.4	93.5	"	300	900
" 19	76	22.2	72	8.0	84.3	S. v. E.	300	800
" 20	68	24.0	74	9.0	76.1	N. E.	300	800
" 21	69	12.2	73	5.6	87.2	"	300	700
" 22	70	26.6	71	9.2	81.3	"	300	600
" 23	68	25.2	73	9.2	73.5	"	300	500
" 24	69	12.0	73	6.2	84.4	S.	300	500

These data were taken with the assistance of our field assistant, E. G. Clarke.

November 24, or seven and one-fourth months from the date of planting the cane, the experiment was stopped. The growth was no longer normal, due possibly to the want of room for extension of the root system, and also in part to the moistness of

the soil, which was kept at the point of saturation. At this place, we shall remark that, while tub experiments afford the most exact mode of controlling certain observations, other observations which require a continuance up to actual maturity, cannot be carried out in such restricted conditions. In no case have we found a mature and normal development of the cane when grown in tubs. In normal growth in the field, the roots of the cane are found very many feet away from the stock in their search for food and water.

Before considering further the data bearing on transpiration from the sugar-cane, we shall refer to the comparative proportions of water that were actually dissipated by the "evaporators," and the apparent relation of this evaporation to the "humidity in the air." In order to do this with convenience we shall gather the total data together in a table of averages, bringing them more easily within view :

Memoranda.	April.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	General average.
Mean outdoor temperature..	74.4	76.0	77.0	78.3	78.7	76.8	75.3	71.0	75.9
Mean outdoor evaporation ..	28.5	27.2	22.5	25.8	30.0	24.3	23.5	17.3	24.8
Mean indoor temperature ..	78.7	80.3	81.3	83.0	82.4	80.6	78.8	74.1	79.9
Mean indoor evaporation...	11.7	11.3	10.1	12.1	12.5	10.0	9.2	7.5	10.5
Mean humidity in the air ...	77.4	80.2	83.6	77.3	73.8	80.4	80.1	83.2	79.5

If the "mean indoor evaporation" is considered with the "mean humidity in the air" it is apparent that there is a very clear and strong relationship, although this relationship is not always in a proportional ratio. The relationship is not so definite between the "humidity of the air" and the "mean outdoor evaporation." A corresponding relation is seen between the "mean indoor temperature" and the "indoor evaporation," which is as definite, and equally constant, as the connection between the evaporation and the humidity of the air, indoors. Notwithstanding these relations of the humidity in the air, and of the temperature, to the evaporation, the great difference between the "indoor" and the "outdoor" evaporation indicates that there is some other cause of evaporation whose potency supercedes the combined controlling actions of temperature and atmospheric humidity. This is set forth more strikingly by the following table :

## EVAPORATION AND PLANT-TRANSPIRATION

Evaporators.	Number of days.	Mean temperature.	Humidity of the air.
"Outdoor" or wind exposure	270	75.9	79.5
"Indoor" or no wind .....	270	79.9	79.5

From this table it is seen that the "outdoor" evaporator, which was carefully protected against the sun, yet exposed to the wind, evaporated 136 per cent. more water than the "indoor" evaporator, and yet the mean temperature was 4° higher than the outdoor temperature, while the humidity was the same. These data confirm a statement in a previous publication, that the "direction and force of wind is a more potent factor in increasing or decreasing evaporation, than small variations in temperature."

It is further shown that there is not necessarily a proportional ratio between the "humidity in the air" as shown by the dry- and wet-bulb readings, and the "evaporation." The factor of "wind" dominates the conditions of atmospheric moisture and temperature. The selection of meteorological instruments for recording climatic data has to be borne in mind.

Moreover, in the matter of practical irrigation, not only temperature and the relative state of moisture in the air, but mainly the exposure to wind, are controlling factors in the rate of evaporation, and the proportion of water lost. Consequently for these reasons alone, and apart from the characteristics of the soil, more or less water of irrigation should be applied in certain localities than in others. On the leeward side of islands the temperature is several degrees higher than on the windward exposures. The winds from the south are little more than prolonged calms, excepting when a storm occurs, while the north or northeast winds are of great mean velocity, which causes a high evaporation. The data to the detailed data already given will furnish ample proof of these facts.

Returning to the experiment on evaporation from the cane, in the tubs, we first give the results together in a table of averages. At the head of the table repeat the daily average for each month of the evaporation.

the "indoor" evaporator, in order to note any relation between the variations of evaporations from the soil and from the evaporator. The data furnished by the "indoor" evaporator are selected for this purpose because the tubs were placed so as to be protected from the wind, thus corresponding to the exclusion of the wind from the barn where the evaporator was placed :

Time.	Indoor evaporation. Per cent.	No. 1 tub. Evaporation from the soil. Grams.	No. 2 tub. Transpiration by cane and soil. Grams.
April.....	11.7	15,000	15,100
May .....	11.3	12,290	13,150
June .....	10.1	9,350	15,850
July .....	12.1	12,300	23,300
August .....	12.5	12,200	31,800
September .....	10.0	9,400	30,450
October.....	9.2	9,700	30,800

Between the "indoor evaporation" and the "evaporation from the soil" a relation in behavior is clearly noted.

During the month of April the two tubs evaporated exactly the same volume of water. When the cane began to grow, transpiration supplemented the evaporation from the soil, and No. 2 tub commenced to dissipate more water, increasing the proportion in ratio with the development of the cane.

A decrease in evaporation from the soil, as in June and again in September, has not, during any period, been accompanied by a decrease in transpiration by the cane. Indeed, it has operated in the opposite direction. In September, it is seen, the evaporation from the soil in tub No. 1 was 2,900 grams less than during August; the total transpiration from tub No. 2, however, was only 1,350 grams less in September than in August. As the evaporation from the soil in the two tubs was the same, it then appears that the cane transpired 1,550 grams more in September than in August, although the total loss of water in tub No. 2 was less in September than in the preceding month. This result is quite understandable. During warm, calm, sultry weather, when the moisture in the air is relatively high, plant-growth proceeds rapidly; and as the transpiration is a result of, and in proportion to, the rate of growth, more water can be dissipated by the plant under the particular atmospheric conditions which cause a decrease in evaporation from the soil.

## EVAPORATION AND PLANT-TRANSPIRATION.

We now call attention to one other factor over whose on plant-transpiration we can have a control. On Sept the cane in tub No. 2 was losing its appearance c and vigor ; the leaves began to yellow and to curl up the first stage of withering. Of course there was no qu want of water, neither of the need of potash, phosphoric lime, since the soil is very rich in these elements. ' however, is very low in nitrogen, and it occurred to t that the growth, and consequently the transpiration, w checked by the dearth of that element. Therefore, on ber 24, 100 grams of sodium nitrate (Chili saltpeter) v solved in the water in the pan under tub No. 2, conta growing cane. This was repeated on October 31st, the and transpiration having suffered a second depressio time. The apparent results of the action of nitrogen ar follows :

First application of nitrogen.			Second application of nitro		
Date.	Transpiration		Date.	Tr	
	Evaporation from soil.	from soil and cane.		Evaporation from soil.	Tr
	Grams.	Grams.		Grams.	
Sept. 24	300	800	Oct. 31	300	
" 25	300	900	Nov. 1	300	
" 26	300	900	" 2	300	
" 27	300	1000	" 3	300	
" 28	300	1200	" 4	300	
" 29	300	1500	" 5	300	
" 30	300	1400	" 6	300	
Oct. 1	300	1200	" 7	300	
" 2	300	1200	" 8	300	
" 3	300	1200	" 9	300	

A third application of nitrogen was made on Novem the result of which corresponded with the former, bu growth of the cane was now being affected by the cro the root system in the tub, further data did not appear enough for use.

It is seen that six days after the first application of the transpiration was increased from 800 grams to 150 or nearly 100 per cent. A corresponding effect is n the second application. In looking back over the data it will be seen that these increases in transpiration are and more sudden and marked, than any such that resul

variations in the effects of atmospheric influences. Also, that no appreciable increase in the transpiration occurred without an accompanying increase in evaporation from the soil in tub No. 1.

These observations upon the action of nitrogen in plant-transpiration appear to amply support our practical advices sent out to the managers of sugar plantations during the period of great drought last year. We advised that sodium nitrate should not be applied until after rain came, giving as our reason that the nitrogen would stimulate growth and cause increased transpiration, which would result in the rapid and greater exhaustion of the soil moisture, and a subsequent collapse of the crop, if the drought continued, which experience has shown to be liable in districts upon these islands, and for a period of six to twelve months.

Further, these observations appear to support our view, which is in opposition to the views of distinguished observers; *viz.*, that nitrogen (and not potash or phosphoric acid) is the vital and controlling element in the life and growth of plants. All constituent elements are necessary to this growth, but nitrogen seems to be supremely so. Our view in this matter rested upon the consideration, that nitrogen is a vital and essential constituent of protoplasm; that protoplasm is a component substance of all structural cells, whose development and increase are the explanation of plant-growth. All vegetable organisms contain protoplasm. The higher forms have this nitrogenous, fundamental substance admixed with large proportions of non-nitrogenous matters; but the incipient forms of life have been regarded as little more than drops of the protoplasmic fluid.

At the end of seven and one-fourth months the cane in tub No. 2 was taken up and divided into roots, stems, and leaves, whose proportions of water-free material were as follows:

Roots. Grams.	Stems. Grams.	Leaves. Grams.	Total weight. Grams.
31.8	53.9	483.2	568.9

The water evaporated from the soil in tub No. 1, during seven and one-fourth months, was 83,140 grams. The water evaporated by the soil, and transpired by the cane in tub No. 2, during the same period, was 167,250 grams, thus showing that the cane transpired, during the period between the dates of planting



and cessation of growth, 84,110 grams of water. As the total amount of the dry material produced during the period of growth was 568.9 grams, it is thus shown that for each gram of water-free sugar-cane material produced, 147.8 grams of water were transpired.

It is understood that this experiment is not intended to represent what actually takes place when a crop is grown in exposure to sun and wind. In the field, evaporation decreases as the crop protects the ground from the sun and wind. In these observations the soil in each tub was kept in the same state of exposure, the cane in tub No. 2 being tied up in order not to shade the soil. As the evaporation from the growing crop increases, this increased transpiration is in greater proportion than the decrease in the soil evaporation. The actual evaporation from the cane growing in tub No. 2, during the several months, was as follows :

# THE NATURE OF THE CHANGE FROM VIOLET TO GREEN IN SOLUTIONS OF CHROMIUM SALTS.

BY F. P. VENABLE AND F. W. MILLER.

Received May 5, 1898.

IT is a well-known fact that solutions of certain chromium salts which are violet in color become green on heating. This has been especially noticed in the case of the chrome-alums and of the sulphate, but is also true of the nitrate, chloride, and acetate, in fact, of all the soluble compounds of chromium. A reverse reaction also takes place and all of these solutions made green by heating become violet again on standing, the nitrate, chloride, and acetate very rapidly, the sulphate and alums slowly, and often only after prolonged standing. It is quite reasonable to suppose that these changes are caused by similar reactions in the case of various salts, and that there is one explanation for all.

A large number of explanations have been offered by various investigators. In fact it is surprising to find how many have been drawn to investigate these changes and what an amount of work has been done upon them. Perhaps the difficult nature of the problem has been the great source of attraction. Fischer<sup>1</sup> and Jacquelin<sup>2</sup> have attributed these changes to a separation of the chromium sulphate from the alkaline sulphate; Berzelius<sup>3</sup> and Fremy<sup>4</sup> assigned as the cause of the changes the formation of a basic sulphate; Recoura and Whitney<sup>5</sup> and Dougal<sup>6</sup> have considered the true cause to be the formation of a chrom-sulphuric acid; Schrötter<sup>7</sup> suggested a partial dehydration, and Etard<sup>8</sup> also thought the change due to an alteration in hydration; Roscoe and Schorlemmer<sup>9</sup> regarded the green solutions as containing mixtures of basic and acid salts; Loewel<sup>10</sup> advanced the theory of an isomeric change.

<sup>1</sup> Kastner's *Archiv.*, 14, 164.

<sup>2</sup> *Compt. rend.*, 24, 439.

<sup>3</sup> *Ann. phys. Chem.*, 61, 1.

<sup>4</sup> *Compt. rend.*, 47, 883.

<sup>5</sup> *Ztschr. phys. Chem.*, 1896, 20, 40.

<sup>6</sup> *J. Chem. Soc., Lond.*, 1896, 69, 1526.

<sup>7</sup> *Pogg. Ann.*, 53, 513.

<sup>8</sup> *Compt. rend.*, 84, 1090.

<sup>9</sup> *Treatise on Chemistry*, First Edition, Vol. II, Pt. II, 163.

<sup>10</sup> *J. d. Pharm.* (3), 7, 321.

## CHANGE OF COLOR IN SOLUTIONS OF CHROMIUM

It is quite manifest that any theory like that of J. Jacquelin, based upon an examination of the alum is quite inadequate. It is further evident that any process which has aroused so great a variety of speculation must be considered very carefully with due weighing of known fact. These facts are numerous and important.

### HOW THE CHANGE MAY BE BROUGHT ABOUT

Chrome-alum is soluble in six parts of water; the solution suffers the alum slowly to crystallize out upon spontaneous evaporation; but if heated to between 50° and 60° it turns green and, according to the extent of decomposition, either deposits on evaporation a brilliant, green, and difficultly soluble mass, or "yields crystals of sulphate leaving green sulphate of chromic oxide in solution.

Schrötter says the change takes place at 65°–70°. He states that the crystals of potassium sulphate separate from a highly concentrated solution and in small quantity has shown, in experiments to be quoted later, that the change begins at a temperature under 30°.

We have repeatedly attempted to secure the separation of crystals of potassium sulphate as described by J. Schrötter, but without success. The exact conditions are clearly difficult to hit upon, if such a separation is possible.

Alkaline hydroxides and carbonates, according to Etard<sup>1</sup> turn violet solutions of the alums green, and Etard<sup>2</sup> states that they bring about the same change in solutions of chromic sulphate. Sulphuric acid, phosphorus trichloride, and nitric acid, according to Etard, bring about the same change, but Otto<sup>4</sup> says that sulphuric acid does not turn solution of alum green if rise of temperature is prevented. Schrötter states that nitric acid turns green solutions of chromium sulphate again.

Our experiments along this line resulted as follows: to the action of acids. Hydrochloric acid had no effect.

<sup>1</sup> Fischer, cited in Gmelin: Handbuch, 1850, IV, 149.

<sup>2</sup> *J. prakt. Chem.* (2), 23, 58.

<sup>3</sup> *Compt. rend.*, 84, 1090.

<sup>4</sup> Graham-Otto, 4 Aufl. 3, 113.

Date, 1897.		Mean outdoor evaporation.	Outdoor evap- oration.	Mean indoor temperature.	Indoor evapo- ration.	Humidity.	Direction of wind.	Evaporation of soil No. I.  Saturated. cc.	Evaporation of soil and cane No. II.  Cane planted. Saturated. cc.
July	19	78	23.0	81	10.6	81.9	E.	400	700
"	20	76	23.0	81	10.0	81.9	N. E.	400	700
"	21	79	27.6	83	13.0	74.1	E.	400	700
"	22	78	25.4	82	12.0	74.0	"	400	700
"	23	79	29.0	82	12.0	76.6	"	400	700
"	24	79	29.0	84	14.0	71.7	"	400	700
"	25	79	20.6	84	11.2	71.7	"	400	700
"	26	80	28.0	83	12.2	74.2	"	400	700
"	27	79	28.8	83	13.2	74.1	"	400	700
"	28	79	32.2	84	15.2	76.7	"	400	800
"	29	78	25.2	83	12.0	76.7	"	400	800
"	30	77	26.0	84	12.8	76.7	E. S. E.	400	800
"	31	78	31.0	84	14.0	76.7	E.	400	800
Aug.	1	77	24.2	84	12.0	76.7	"	400	800
"	2	76	17.6	83	11.6	79.1	S. E.	400	800
"	3	79	18.2	85	11.0	76.7	"	400	800
"	4	80	23.0	86	12.0	76.8	E.	400	800
"	5	78	23.6	83	11.2	79.2	"	400	800
"	6	78	32.6	83	13.8	76.7	"	300	700
"	7	77	31.0	81	12.2	81.8	"	400	700
"	8	78	30.2	81	12.6	76.5	N. E.	400	800
"	9	79	31.6	84	14.0	71.7	"	400	800
"	10	79	26.2	84	13.0	71.7	E.	400	800
"	11	78	27.2	83	12.2	71.7	"	400	800
"	12	79	23.0	83	10.8	79.1	"	400	800
"	13	80	15.0	83	7.6	84.8	"	400	800
"	14	80	25.4	84	11.2	82.1	"	400	800
"	15	79	26.6	82	12.2	71.6	"	400	800
"	16	77	31.2	83	13.4	71.7	"	400	800
"	17	78	26.2	81	12.0	74.0	"	400	800
"	18	79	32.2	84	12.4	71.7	"	400	800
"	19	80	33.0	83	13.2	74.1	"	400	900
"	20	79	26.0	83	13.2	71.6	"	400	900
"	21	78	26.0	81	13.0	74.0	"	400	1000
"	22	78	26.0	82	12.0	74.0	"	400	1000
"	23	81	33.4	84	15.8	69.3	"	400	1000
"	24	80	29.6	84	14.4	74.2	N. E.	400	1000

! One stalk of cane died.

Date, 1877.		Mean outdoor evaporation.	Outdoor evap- oration.	Mean indoor temperature	Indoor evapo- ration.	Humidity.	Direction of wind.	Evaporation of soil No. I	Evaporation of soil and cane No. II.
								Saturated. cc.	Saturated. Cane planted. cc.
Aug.	25	79	30.6	83	14.0	74.1	E.	400	1000
"	26	79	26.4	80	12.6	76.6	"	400	1000
"	27	80	25.6	83	13.0	74.2	"	400	1000
"	28	80	26.0	83	12.0	76.7	"	400	1000
"	29	79	31.6	83	14.2	71.7	"	400	1000
"	30	79	32.6	83	13.6	71.6	"	400	1100
"	31	79	35.2	83	14.0	67.0	"	400	1100
Sept.	1	78	29.0	82	12.0	74.0	N. E.	400	1200
"	2	78	32.6	81	11.6	84.6	"	400	1200
"	3	79	32.0	84	13.6	69.3	"	400	1200
"	4	78	34.0	82	13.0	74.0	"	400	1200
"	5	79	35.0	83	13.0	71.6	"	400	1200
"	6	79	27.4	82	11.2	74.1	"	400	1200
"	7	79	31.8	83	12.0	76.6	"	400	1100
"	8	79	32.8	83	11.6	71.6	"	400	1100
"	9	79	26.2	84	9.0	72.2	"	400	1000
"	10	80	23.0	82	10.6	84.7	"	400	1000
"	11	79	39.0	83	14.6	71.6	E.	400	1000
"	12	78	31.0	83	12.0	69.3	N. E.	400	1000
"	13	77	28.2	79	10.2	79.0	"	400	1000
"	14	77	30.2	79	10.0	76.5	"	400	1000
"	15	76	28.2	81	11.8	71.5	"	400	1000
"	16	75	25.0	81	11.4	71.6	"	400	1000

barium chloride, yields practically all of its sulphuric acid as barium sulphate. A cold green solution forms a precipitate slowly, and even after a number of hours the precipitation is far from complete. On boiling, all of the sulphuric acid will be precipitated. Favre and Valson found that only one-third of the sulphuric acid present in the original chromic sulphate was precipitated in the cold by the barium chloride.

Our own experiments upon this point were as follows: A weighed amount of the pure alum was dissolved and the solution made up to a definite quantity. Two aliquot portions were taken, one of which was heated for half an hour and allowed to cool. Then both portions were precipitated with an excess of barium chloride. It was found impossible to filter these immediately with asbestos felts or the best filter-paper. They were therefore allowed to stand about twenty-four hours. This very long standing probably changed the conditions somewhat, but we were unable to avoid it. Still the results would confirm the observations of Favre and Valson. The prolonged standing also showed that it was not merely a delayed precipitation, but one partially prevented.

	I.	II.
Percentage of $\text{SO}_3$ in alum is 32.06 .....	....	....
Percentage of $\text{SO}_3$ in alum, violet solution precipitated cold .....	30.44	30.19
Percentage of $\text{SO}_3$ in alum, green solution heated one-half hour .....	22.78	22.33
Percentage of $\text{SO}_3$ in alum, green solution heated one hour .....	22.87	21.83

These experiments were upon solutions containing one gram to 100 cc. A solution twice as strong was next taken:

	I.	II.
Percentage in violet solution precipitated cold .....	28.88	31.80
Percentage in green solution (heated one hour) precipitated cold .....	19.55	21.47

Again a solution containing 0.5 gram to the 100 cc. was taken.

Percentage in violet solution precipitated cold .....	28.30
Percentage in green solution (heated one hour) precipitated cold .....	23.00

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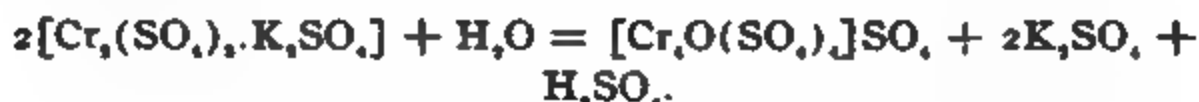
## THE EXISTENCE OF CHROMO-SULPHURIC ACIDS.

Several articles have been published by Recoura<sup>1</sup> upon chromo-sulphuric acids. He claims to have prepared several of these and regards the formation of such bodies as a probable explanation of the change in the green solutions, and others, as Whitney and Dougal, seem to accept his explanation. Recoura thinks there are two isomeric modifications of chromium sulphate; one violet, one green, and also another green sulphate not isomeric, but basic ( $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_3$ ). These he refers to three conditions of chromic hydroxide:  $\text{Cr}_2(\text{OH})_6$ , precipitated by alkalies from violet chromic salts;  $\text{Cr}_2\text{O}(\text{OH})_4$ , corresponding to the basic sulphate and non-isolable;  $\text{Cr}_2\text{O}(\text{OH})_4$ , precipitated by alkalies from green solutions. Solutions of this latter in acids, he says, are not precipitated by solutions of barium salts. This last statement is not strictly true. Such solutions are partially precipitated by barium salts just as all green solutions are. He assigns to the green sulphate the formula  $\text{Cr}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 11\text{H}_2\text{O}$ , which he says has quite a different constitution from that of the violet sulphate. Proofs for this statement he does not give. This isomeric green sulphate, he says, possesses neither the characteristics of a sulphate nor of a chromium salt. One molecule can combine with one molecule of either sulphuric acid or a metallic sulphate. Thus we may have  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4$ , or  $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4$ . In these compounds all the sulphuric acid is in a non-precipitable form, he maintains. His crucial experiment is as follows:

“Mix a solution containing one molecule of  $\text{Cr}_2(\text{SO}_4)_3$  with a solution containing one molecule of sulphuric acid or a sulphate. Union is immediate, for barium chloride will now give no precipitate and the solution therefore holds no sulphate. The new radical is unstable, for precipitation is immediate on boiling, or

On such slender basis Recoura builds up a series of salts of a hypothetical chromo-sulphuric acid  $(Cr_2.4SO_3)H_2$ . He has also prepared a chromo-disulphuric acid, chromo-trisulphuric acid, etc., by evaporating solutions of chromium sulphate with two, three, etc., molecules of sulphuric acid, and then heating to  $110^\circ$ - $120^\circ$ . Calvert and Ewart<sup>1</sup> have shown that, on dialyzing these, they all leave a colloidal  $Cr_2(SO_3)_3.H_2SO_4$  upon the septum, the liquid passing through free of chromium. The behavior of these solutions makes it appear probable that the chromo-sulphuric acids do not exist in them as such, but are hydrolyzed, forming a colloidal substance,  $Cr_2(SO_3)_3.H_2SO_4$ , and free sulphuric acid. Our repeated experiments have failed to show the presence of this colloidal body in the ordinary green solutions of the alum or sulphate. A boiled solution of either, even though very concentrated, will pass entirely through an unglazed porcelain suction filter, such as Calvert and Ewart made use of. There seems to be no colloidal body present.

We cannot regard the experiments of Recoura as advancing the knowledge of the subject in any degree. As an explanation of the changes it is by no means satisfactory. Dougal's formula for the reaction causing the change, is even more remarkable and baseless:



This is not based upon Dougal's own experiments but is offered as an explanation deduced from the work of Recoura, Whitney, Favre, and Valson.

#### THE ACTION OF ALCOHOL.

There have been several investigations of the action of alcohol, both upon the sulphate and the alum, with the hope of throwing some light upon the changes under consideration. Traube<sup>2</sup> states that the solid salt is unaffected by boiling alcohol. Schrötter has observed<sup>3</sup> that solutions covered with a layer of alcohol became gradually green and the concentrated green solution is not dissolved by alcohol. Of course the first obser-

<sup>1</sup> *Chem. News*, 74, 121.

<sup>2</sup> *Ann. Chem. (Liebig)*, 66, 168.

<sup>3</sup> *Pogg. Ann.*, 53, 513.

## CHANGE OF COLOR IN SOLUTIONS OF CHROMI

vation does not necessarily connect the alcohol w  
Alcohol in large amounts precipitates from violet  
sulphate a pale violet colored, crystalline powde  
izes the liquid.<sup>1</sup> This can be used as a mode of  
alum.<sup>2</sup> Siewert<sup>3</sup> states that, when the violet sulph  
in a small amount of water and boiled with alc  
crystals formed are again taken up and then pr  
ether, a green syrup is gotten which consists of  $5\text{Cr}_2$   
and the mother-liquor contains sulphuric acid in  
which it is not precipitated by barium chloride.  
that alcohol precipitates from a green solution  
green oil which solidifies and which contains only  
the sulphuric acid. Siewert confirms this and say  
stance has approximately the composition  $6\text{K}_2\text{O}$   
 $\text{H}_2\text{O}$ . Krüger mentioned the acidity of the alcol  
cipitating the green oily liquid and evidently  
withdrawing sulphuric acid from the original  
mentioned the formation of a basic salt, by heat  
solution until it becomes rose-red, which contains  
acid as the neutral salt and is insoluble in water.

After a careful consideration of the results obta  
by means of alcohol, it seemed to us quite possi  
might afford a clue to the explanation we were in  
was necessary to examine with care the action  
violet and the green solutions. Our experiments  
given in detail, and it will be seen that they agree  
with the observations just quoted.

*Action on the Violet Solutions.*—When alcohol  
the violet solution of the alum, fine violet crystals  
tated, which gave on analysis the following result

	Calculated for $\text{K}_2\text{Cr}_2(\text{SO}_4)_4 \cdot 12\text{H}_2\text{O}$ .	I. F
Cr .....	13.32	13.68
K.....	9.99	9.80
$\text{SO}_4$ .....	49.99	48.85

This may be an old observation that on cry  
alcohol the crystals contain only half the usual an

<sup>1</sup> Gmelin's Handbuch, IV, 127.

<sup>2</sup> Baubigny and Pechard: *Loc. cit.*

<sup>3</sup> *Ann. Chem.* (Liebig), 126, 97.

<sup>4</sup> *Ann. phys. Chem.*, 61, 218.

but we have not met with it anywhere. The fact that this very considerable change of hydration effects no change in color nor in the precipitating power of barium chloride, argues against the partial dehydration theory of Schrötter and Etard. It should be added that the precipitation was carried out with absolute alcohol upon concentrated solutions of the alum, was rapid, and the precipitate was immediately removed. There seemed to be two layers of crystals, one of violet crystals, and the other (upper) one of a fine heliotrope power. Analysis showed that the composition of both was the same, and that the difference was probably one of subdivision. The precipitation is almost complete, as the alcohol shows very little color. From this it is evident that alcohol itself does not materially affect the violet solutions.

*Action on the Green Solutions.*—Green solutions of the alum were first experimented with. When absolute alcohol is added to concentrated solutions of chrome alum, which have been boiled until fully green and allowed to cool, a dark green gummy mass separates out after a short time. If the boiling is not sufficiently prolonged there will form afterwards a few violet crystals. The alcohol retains something in solution, as is shown by the green color. This amount retained may be considerable if much water is present. It would seem then, that alcohol precipitates out the body formed by the boiling and makes it available for analysis and examination. If a portion of this green, gummy mass is taken and dissolved in water, it exhibits the same behavior towards barium chloride as has been observed in the green solutions. In one or two cases it was observed that the part remaining dissolved in the alcohol yielded practically all of its sulphuric acid to barium chloride in the cold. The green mass was thoroughly washed with alcohol and dried over sulphuric acid. It also dries to a brittle mass if exposed in thin layers to the atmosphere. It is quite insoluble in alcohol, but soluble in water. A number of preparations of this substance were made and analyzed and the results are in such agreement that one is inclined to believe that the substance is a definite compound.

Fifteen grams of chrome alum were dissolved in 100 cc. water

and boiled for one hour to a concentration of fifty cc. This was cooled and precipitated by the addition of 100 cc. of absolute alcohol. The green mass obtained on drying weighed about eight grams. This was carefully analyzed :

	Calculated for $7K_2SO_4 \cdot 5Cr_2(SO_4)_3 \cdot Cr_2(OH)_4 \cdot 4H_2O$ .	I.	Found II.	III.	IV.
Cr.....	18.07	18.23	18.32	18.02	17.76
K .....	15.88	15.18	15.63	15.78	....
SO <sub>4</sub> .....	61.08	60.55	60.73	....	60.79

Analysis III and IV were from other preparations, made, however, in a similar manner to that just described. This substance appears to have quite a complicated constitution, and it is not easy to see the part played by the potassium sulphate. It does not seem to be a matter of accidental occurrence, however. The important feature is that the salt is a basic one. Siewert gives, as the result of his analysis,  $6K_2O \cdot 5Cr_2O_3 \cdot 18SO_3 \cdot H_2O$ , for which the following percentages would be required: Cr, 18.7; K, 16.8; SO<sub>4</sub>, 61.9. While these percentages differ somewhat from those obtained by us, the agreement is sufficiently close to show that the substances examined were practically the same.

On concentrating the liquid poured off from the green gum, it was repeatedly observed that more of the gum was obtained. For instance, in the experiment described where the green mass from fifteen grams weighed about eight grams, a further portion weighing 0.3915 gram was gotten. The analysis of this yielded the following percentages: Cr, 13.66; K, 8.57; and SO<sub>4</sub>, 55.45.

color. Fifteen grams of this dissolved in 100 cc. of water, boiled to a concentration of 50 cc. and precipitated with 100 cc. of alcohol, yielded about ten grams of the green, gummy mass, very similar in appearance to that obtained from the alum, but more soluble in alcohol. In a second experiment twelve grams were taken and treated in the same way, and yielded about eight grams. The analysis showed these to be identical.

	Calculated for $\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Cr}_2(\text{OH})_4 \cdot 15\text{H}_2\text{O}$ .	I.	Found. II.	III.
Cr.....	24.06	22.41	22.40	22.69
SO <sub>4</sub> .....	33.17	34.64	34.73	34.43
Water .....	43.77	....	....	....

The agreement is far from satisfactory, but the body is evidently a basic salt.

On evaporating the liquid portions other masses were obtained. These were also analyzed :

	Calculated for $2\text{Cr}_2(\text{SO}_4)_3 \cdot \text{Cr}_2(\text{OH})_4 \cdot 20\text{H}_2\text{O}$ .	I.	Found. II.	III.
Cr.....	22.70	22.93	22.71	22.98
SO <sub>4</sub> .....	42.72	43.71	42.32	43.46
Water .....	34.57	....	....	....

This is less basic than the previous compound. As the alcohol left is decidedly acid, it must contain either free acid or an acid sulphate.

## ORGANIC MATTER IN WATER.

The theory of Berzelius, however, of the formation of salts of chromium which would naturally be green and is in accord with the observations so far as they are verified by us. It accounts quite plausibly for the holding of the sulphuric acid from precipitation by oxide in the cold, and is strongly confirmed by the experiment with alcohol. This theory is also in accord with the observation that the green coloration may be brought about by the

The fact that by means of the Forchhammer process as ordinarily carried out we are unable to distinguish the character of the organic matter contained in water, has been recognized by nearly all chemists who are authorities upon the subject of water analysis. Frankland<sup>1</sup> says in regard to this: "Reliance ought not to be placed on the Forchhammer process, for the action of the permanganate of potash test is not only liable to considerable uncertainty, but it makes no distinction between nitrogenous and non-nitrogenous organic matter, and may even confuse innocent inorganic substances with organic matters of most objectionable origin." It is true that methods have been proposed by which this distinction may be more or less satisfactorily made, but most of those which do not require an excessive amount of time and care in manipulation are matters of judgment rather than of determination. Dr. Tidy, for example, proposes to judge the character of the organic matter by an examination of the "tint and tint depth" of the water through a two-foot tube. Considerable work has been done in this laboratory and elsewhere in order to replace the potassium permanganate by chromic acid, but it was always found that the oxidation was still incomplete.

A method for distinguishing the different kinds of organic matter by the use of chromic acid in comparison with potassium permanganate has quite recently been proposed by Joseph Barnes.<sup>2</sup> He expresses the results in the form of a ratio between the oxygen consumed from permanganate and that taken from chromic acid. The results obtained show that solutions of starch and of sugar are acted upon by chromic acid to a much greater degree than by permanganate, thus giving a very low ratio. Gelatin and glycerol in dilute solutions are likewise found to give a fairly low ratio. The highest ratios were given by infusions of peat and of tannic acid. In this work the method suggested by Barnes has been applied to the determination of organic matter in water.

The method used, while essentially that of Barnes, differs from it in some important particulars, and will be described in considerable detail because the results obtained depend largely

<sup>1</sup> *Water Analysis*, 1890.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1896, 83.



## ORGANIC MATTER IN WATER.

upon the method of procedure that is adopted. The oxidation of the carbonaceous matter is first made with potassium permanganate according to Kubel's hot acid method. To a measured quantity of the water, usually 100 cc. in a 250 cc. flask, are added eight cc. of sulphuric acid, and then about ten cc. of  $\frac{N}{100}$  potassium permanganate, until the water is highly colored, are added from a burette. The solution is heated to boiling and boiled for exactly five minutes, then allowed to cool for one minute, and the pink color is destroyed by ten cc. of  $\frac{N}{100}$  oxalic acid. It is then titrated with  $\frac{N}{100}$  potassium permanganate to the usual faint pink color. If one wishes to apply the chromic acid method, the following specifications are required: (a) six and two-tenths grams of potassium dichromate are dissolved in distilled water, fifty cc. of concentrated sulphuric acid added, and the solution is made up to 100 cc. (b) eighteen grams of crystallized ferrous sulphate are dissolved in a mixture of 100 cc. concentrated sulphuric acid and 100 cc. water. When cool the solution is diluted to 500 cc. The solution will not keep for more than two or three weeks. Portions of the water under examination are placed in a 250

being used as public supplies, and to filtered city sewage in various degrees of dilution. The results obtained on these "peaty waters" are tabulated below. The "ratio" is obtained in the form of a fraction as mentioned above; the colors given are based on Professor Leeds' nesslerized ammonia scale.

	Color.	Ratio.
Boston tap water July 24, 1897: .....	0.3	0.656
" " " Jan. 24, 1898. ....	0.7	0.646
" " " Mar. 11, 1898 .....	0.48	0.649
Color standard 'a' .....	5.00	0.833
Color standard 'b' .....	1.8	0.689
Reservoir, Orange, Mass. ....	0.58	0.659
" Athol, " full of algae) .....	.....	1.132
" " " filtered .....	1.7	0.750
Infusion of dried leaves .....	about 10.0	0.656
Solution of humus in ammonia .....	.....	0.692

The Boston tap water is a typical brown surface water. The color standards are very dark-colored swamp waters of different dilutions. The waters from Orange and from Athol were surface waters which contained so great a growth of algae, especially *Anabaena*, as to be colored distinctly green, and gave extremely high "oxygen-consumed" and albuminoid ammonia. The leaf infusion was made by treating the dried leaves with cold distilled water, the first portion, containing the sugary extract, being rejected. It had been standing about ten months.

The ratios obtained with sewage, as shown in the following table, are about the same as given by Barnes for nitrogenous substances.

	Ratio.
Sewage from Marlboro (filtered, old) .....	0.543
" " Boston (decanted, fresh) .....	0.389
(a) Filtered sewage, Hereford St., Boston ....	0.470
(b) Sewage (a) diluted five times with distilled water .....	0.490
(c) " (a) " ten " " " " " " .....	0.460
Well contaminated with sewage .....	0.449

Two things are evident from the results shown in the foregoing tables. First, the peaty waters give a ratio above 0.600; the sewage and sewage-contaminated waters give a ratio below 0.600, this apparently being the dividing line between the ratios of animal and vegetable matter. Second, the ratio for a given water is practically constant if the character of the organic

## EFFICIENT GAS-PRESSURE REGULATOR.

matter present does not undergo material change, no much the amount present may vary. The results of tap water at intervals of several months and with conditions of the same sewage show this. In order to test this, and to see if it were really possible to determine organic matter in water by this means, the following experiment was made. Two samples of water were prepared, one (a) was known to be free from sewage but contained a small amount of coloring-matter of vegetable origin; the other distilled water containing a definite quantity of sewage gave the same amount of oxygen consumed by the permanganate process,  $(a) = 0.2387$  and  $(b) = 0.2375$  parts per million. The ratios, however, differed widely,  $(a) = 0.827$ ,  $(b) = 0.372$ . The method was also tried on a sample of water which gave by the permanganate test more oxygen than was warranted by its color. The question to be determined was whether the organic matter was due to sewage infiltration of surface water carrying vegetable matter. The ratio obtained was high, 0.957, indicating that surface water was the cause. This was confirmed later by a chemical analysis of the well. These results certainly show that the method is quite promising and deserves further study by those who are especially interested in the question of sanitary analysis.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
APRIL 20, 1898.

## AN EFFICIENT GAS-PRESSURE REGULATOR

BY PAUL MURRILL.

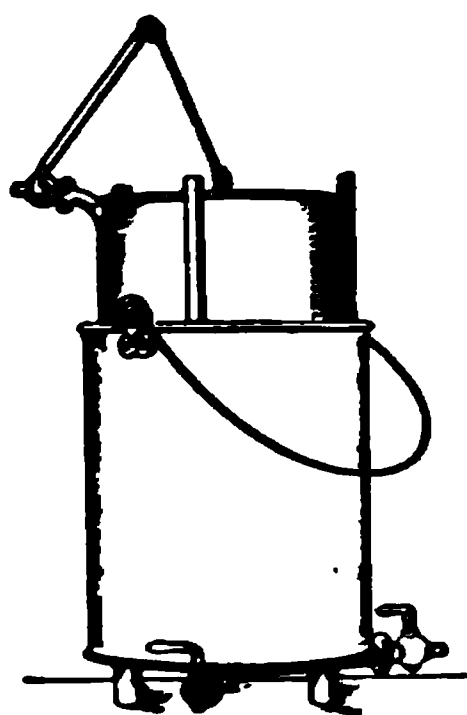
Received April 18, 1898.

IT is well known that the various types of mercury regulators cannot cope with marked changes in pressure, and for this reason it is almost impossible to maintain a constant temperature for a considerable length of time with any degree of certainty. Numerous contrivances for regulating the pressure have been proposed at various times, and they are to be had from the principal dealers, but they are entirely inoperative in their purpose, or are impracticable for use on account of cost, difficulties of construction, etc. The regulator of Moitessier, as catalogued in this country and Europe

to have some features in common with the one described below, but its cost bars it from general use. The Girond rheometer, as modified by Schiff,<sup>1</sup> was tested in connection with a mercury thermostat, with results showing it to be useless for that purpose. A pressure regulator made of glass, described by Schiff,<sup>2</sup> is quite similar in principle to the one here described, but has the disadvantages of being quite fragile, besides requiring skilled glass-blowing in its construction. An apparatus by Knudsen is also described,<sup>3</sup> but is too complicated to be practical.

Having experienced the same difficulties that many other workers have, the attempt was made to devise a simple apparatus which would deliver gas at constant pressure regardless of the various changes of pressure in the gas-pipes. The apparatus having proved satisfactory, a description of it is given. Its strong points are efficiency, simplicity, durability, and cheapness. It can be made of sheet metal, preferably copper, by any sheet-metal worker, or may be obtained from the Eberbach Hardware Co., Ann Arbor, Mich., at a cost of \$3.00, or may even be constructed of glass, using articles found in almost every laboratory. It is designed to be used in connection with a thermostat, and with it the temperature may be held constant within 0.1° C. Using the regulator here described, Prof. F. G. Novy has succeeded in maintaining constant temperatures in an air-bath at 50° and an oven at 150° at the same time.

The dimensions can be varied to suit the purpose of the operator, but those here given will be found suited to the usual needs. The outer vessel or pail is fifteen cm. in diameter and eighteen cm. deep. Through the center of the bottom three tubes enter, rising 14.5 cm. above the bottom. Beneath it the tubes bend at right angles, and diverge or may be run horizontally in any convenient direction. Two of these run a short distance beyond the vessel, terminating in stop-cocks, and serve as exit tubes for the gas. The third, which is the inlet tube, bends upward at the lower edge, and extends eight cm.



<sup>1</sup> *Ber. d. chem. Ges.*, 1885, 2833; *Ztschr. anal. Chem.*, 1886, 385.

<sup>2</sup> *Ztschr. anal. Chem.*, 1886, 383.

(three inches) above the top of the out at right angles again, and terminates in a stop-cock placed horizontally. To this stop-cock a ten cm. lever arm is attached. On the inside of the vessel three vertical U-shaped grooves are soldered, extending eight cm. above the top. The tubing should be less than seven mm. into

inner vessel or gas container  
cm. in diameter and

. On the outside the  
grooves are soldered, corresponding to the three grooves in the inner vessel and projecting sufficiently for rotation or lateral

movement. It is to move freely. The inner vessel is soldered at the end of the lever-arm.

A stiff wire of steel is attached to the inner vessel with attachments eight cm. above the gas

by means of a tube at which laboratory heating

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l on a water

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external diameter a little less than half the difference between the internal diameter of the large jar and the external diameter of the small one, and should extend ten cm. above the top of the outer vessel, serving instead of the flanges and grooves. A glass stop-cock with as large capacity as possible is clamped rigidly in convenient position above the apparatus, and to it a lever arm of light wood is bound. To the end of the arm another light sliver or a wire is attached, which rests on the float and operates the valve.

Operation of regulator is as follows: One of the exit tubes may be connected to a manometer, or both may go to burners as may be desired. Gas enters through the stop-cock and long tube into the container, and in so doing lifts the container, at the same time closing the valve. If outlets are closed the container will rise until the valve is entirely closed, in which position it will stand. When the exit tubes are opened the container falls, re-opening the valve, admitting gas at the same rate at which it is consumed, and delivering it at a pressure which is measured by *the weight of the inner vessel, plus or minus the resistance due to friction*. If the apparatus is well made the resistance amounts to only one or two mm. on the manometer, and it is only exerted during the changes of position of the container. If the pressure in the pipes falls to that in the apparatus, the float falls to the bottom, opening the valve to its fullest capacity, and allowing the gas to flow through unhindered.

Thanks are expressed to Mr. J. T. Faig for the sketches herewith given, and to Professors P. C. Freer and F. G. Novy for assistance rendered in various ways.

LABORATORY OF GENERAL CHEMISTRY,  
UNIVERSITY OF MICHIGAN, ANN  
ARBOR, APRIL 14, 1898.

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## USE OF HYDROFLUORIC ACID IN THE DETERMINATION OF MANGANESE IN IRON AND ORES.

BY ALLEN P. FORD AND I. M. BREGOWSKY.

Received May 13, 1898.

WILLIAMS' method for the determination of manganese is not faultless but is nevertheless the best method for the iron chemist who has to determine manganese in iron, steel, ferro-manganese, and ores.

discovered that hydrofluoric acid plays a much more important part than had been anticipated. In working ores it has always been found that the first addition of potassium chlorate did not completely precipitate the manganese, and after filtering, a second precipitation, and sometimes a third, was made in the filtrate. In the case of the ores above mentioned it was decided to use hydrofluoric acid on one of the samples to see if it would prove as beneficial as in the case of pig iron. On adding potassium chlorate to the filtrate, as in the other cases, no precipitate of manganese dioxide appeared, and this led to further experiments which proved, at least as far as this particular lot of ores was concerned, that the addition of hydrofluoric acid renders the first precipitation by potassium chlorate complete. In this case, as in the case of pig iron, only a few drops of acid were added a few minutes after the potassium chlorate. After a little practice one can judge by the amount of floating gelatinous silica about how much hydrofluoric acid to add. If the first addition does not clear the solution in a minute or two a few drops more can be added.

In beginning the use of the acid with pig irons, it was added to the solution and the silicon eliminated before the manganese was precipitated, as directed by Blair; but some bad results were obtained about this time, and knowing that some reagents will prevent a precipitation while they will not dissolve the precipitate after it is formed, the acid was used as above stated. The bad results may or may not have been due to this, but as it is just as easy to add the acid after the precipitation as before, it has always been so done. We have had long experience with the use of this acid in working pig iron and know it is safe and advantageous. Our work on ores is very limited, but as it appears to be even more useful in this class of work, we take pleasure in bringing it to the attention of those in this particular line of work.

In regard to the effect of the acid on the beakers, although it etches and blurs them, they have been used in this laboratory every day for a period of five or six months. The lower part of the beakers become partially opaque and not suitable for most other work, but by keeping a number of beakers for manganese determinations only, their life will be found to be very little diminished, provided the hydrofluoric acid is used carefully.

## A NEW BACTERIA COUNTER

BY WILLIAM F. MASON.

Received March 15, 1898.

THE "Miller-McPherson" counting apparatus for determining the number of colonies of bacterium in culture media, needs but little explanation beyond the illustration shown herewith.

The "Wolffhüggle" device which is still employed, has the disadvantage of not firmly fixing the dish in place, so that there is no small danger of disturbing the colonies more than once. Nor is it possible to use a "Miquel" flask as a substitute for the "Wolffhüggle" counter is to be employed.

The new apparatus, illustrated herewith, is so constructed that the ruled glass plate is a fixture, while the dish rests upon a movable ebonite plate, which is rotated by the wheel beneath it actuating a hollow screw. The dish may be thus always kept firmly against the ruled plate with no chance of slipping, and moreover it will be so held no matter what may be its thickness.

It is my present practice to almost uniformly use the "Miquel" flask (see illustration) rather than the "Wolffhüggle" because the "plating" can be done in the field and no transportation of the water sample is required.

<sup>1</sup> Read before the New York Section, March 11, 1898.



Under such circumstances the neck of the inverted flask passes through a hole in the ebonite plate and into the hollow screw, while the wheel beneath raises the bottom of the flask against the ruled plate the same as when a "Petri" dish is employed.

The counting apparatus and also the "Miquel" flasks may be obtained of Eimer and Amend, 211 Third Avenue, New York City.

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## THE DETERMINATION OF LEAD IN ALLOYS.

BY W. E. GARRIGUES.

Received April 21, 1898.

I N the analysis of brass and bronze, the fact that we have only a single practicable method for separating lead is an unusual instance of poverty in the case of so common an element.

While the separation and determination as sulphate is admittedly excellent, there is always a more or less lengthy wait during evaporation of the filtrate from the metastannic acid, not to mention occasional losses of the assay at this stage through breakage. The latter is fortunately of rare occurrence and the former of little moment under ordinary circumstances, as no personal supervision is exacted during the operation, but it is not at all a rare occurrence that the foundryman wants his result at the earliest possible moment and it is for such occasions that the following method is especially suited. Nevertheless, the determination is fully as accurate as that with sulphuric acid and as it requires no more manipulation there is no reason why the method should not be employed at all times when the filtrate from the lead is not needed for other determinations.

The precipitation of lead as chromate, from neutral or acetic solutions, is an old and admirable process but it is inapplicable as a separation from copper, the latter being likewise thrown down. Copper chromate is known to be readily soluble in ammonia, but the writer has been unable to find any record of the behavior of ammonia toward lead chromate, the nearest approach being the statement that fixed caustic alkalies decompose it.

Experiment demonstrated that lead chromate is unaffected by

ammonia and confirmed the ready solubility of c  
Hence the perfect separation.

*The Analysis :* To the nitric acid solution of copper, is added an excess of potassium bichromate and ammonia in decided excess. After heating until the liquid clears, the precipitate of lead chromate is filtered in a Gooch crucible (the filtering medium being filter-paper), washed respectively with dilute water, and alcohol, and dried in the water-oven. The results, in practice, have been found

In using the process, it must be remembered that the method is available where the chromate is not essentially a separation from copper and zinc. In the presence of antimony, for instance, it is entirely the small quantity, left in the filtrate from the tin, that is taken down with lead sulphate, by the simple expenditure of a liberal amount of sulphuric acid, diluting sparingly without undue delay. The same applies no doubt to iron. Both of these would obviously appear with the tin. Iron would likewise interfere in the latter case.

Having now described the chromate process, it is more expeditious than the sulphate, there is the serious logical position of having to explain how the reverse is the case inasmuch as the lead can be obtained without the necessity of first removing the tin. The process is delicate and its indiscriminate use may be objected to on good ground with some reason. It, nevertheless, serves to make the separation a clean and satisfactory one, and the observed facts are worthy of being recorded.

The description is perhaps best given in the form of an experiment :

One-half gram of soft solder, containing lead 10 per cent. by the usual sulphate and chromate process, was oxidized with nitric acid, twenty cc. of sulphuric acid added, and the solution evaporated to dense fuming. The metastannic acid was completely removed.

An addition of eighty cc. cold water was made and stirred for a few minutes, and the lead sulphate filtered in a Gooch crucible. The result for lead was fifty-1

The sulphuric acid filtrate was made alkaline with ammonia, again acid with sulphuric, but this time only until it turned methyl orange a decided red. The result was a voluminous white precipitate which was filtered out after boiling the liquid and which, on ignition over the blast, gave stannic oxide, equivalent to 41.1 per cent. tin. Total : 100.1.

If much more than eighty cc. was used for diluting the fuming acid or if the diluted liquid was allowed to stand on the water-bath for an hour or so, the tin began to precipitate slowly.

Antimony, when present in considerable quantity, sustains its reputation by coming down with both tin and lead and partly remaining in the last filtrate besides.

When it is desirable to remove lead and tin in one operation, as for instance in the determination of copper by the writer's thiocyanate method, it is essential to bear in mind the above described behavior of metastannic acid toward sulphuric acid and use the latter very sparingly. There is no difficulty in accomplishing the separation of both together in this manner. One can even go a step farther, in the determination of zinc as phosphate, by oxidizing with nitric acid, expelling the latter with as little sulphuric acid as possible, precipitating the copper as thiocyanate, and removing them all in one filtration. Three per cent. sulphuric-acid washing, to prevent re-solution of lead sulphate, has no effect on either the tin or copper precipitates.

Where small amounts of zinc alone are to be determined in bronze, this procedure is unequalled for accuracy, neatness, and despatch.

THE DUQUESNE CHEMICAL LABORATORY,  
PITTSBURG, PA.

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## INACCURACIES IN THE DETERMINATION OF CARBON AND HYDROGEN OF COMBUSTION.

BY CHARLES F. MABERY.

Received May 16, 1898.

I WAS much interested in the results of Mr. G. Auchy which appeared in the April number of this Journal, since they are closely in line with my own observations in determining these elements in hydrocarbons, and an examination of this subject which I have now in hand. During the last five years in my

work on the composition of the petroleum hydrocarbons, these determinations have occasioned much trouble and expense on account of the difficulty in keeping the details under control. The difficulties which I have encountered are the following :

1. An efficient and durable means for removing carbon dioxide and water from air and oxygen.
2. Maintaining a sufficient temperature to prevent gaseous hydrocarbons from escaping without complete combustion.
3. Incomplete absorption of carbon dioxide in a thirty-three and one-third per cent. solution of potassium hydroxide.
4. Escape of moisture from the potassium hydroxide bulb, over fused calcium chloride and potassium hydroxide.

I now have these details under such control that assistants and students, by following directions, may be sure of obtaining correct results.

It is not the purpose of this note to discuss these details in full since, as mentioned above, I have work in progress for the purpose of ascertaining the limits of these sources of error including the forms of potash bulbs.

That it is not safe to trust to the calcium-chloride attachment of the potash bulb even when it contains solid caustic potash, as ours always does, to retain all moisture, is shown by the following results, in which a second sulphuric-acid tube was placed after the potash bulb. These results are taken at random from notes on combustions recently made :

0.1402 gram of a California distillate,  $138^{\circ}$ – $140^{\circ}$ , gave 0.4485 gram carbon dioxide, and 0.1897 gram water.

	Per cent.
Carbon .....	85.00
Hydrogen .....	14.60

Gain in second sulphuric-acid tube 0.0007 gram.

0.1413 gram of a California distillate gave 0.4372 gram carbon dioxide and 0.1851 gram water.

	Per cent.
Carbon .....	84.84
Hydrogen .....	14.56

Gain in second sulphuric-acid tube 0.0022 gram.

1.1420 grams of a hydrocarbon from commercial paraffin, boil-

ing-point  $306^{\circ}$ – $308^{\circ}$ , fifty mm., gave 0.4134 gram carbon dioxide and 0.1332 gram water.

	Per cent.
Carbon .....	85.19
Hydrogen .....	14.73

Gain in second sulphuric-acid tube 0.0012 gram.

0.1324 gram of a paraffin distillate,  $294^{\circ}$ – $296^{\circ}$ , fifty mm., gave 0.4293 gram carbon dioxide and 0.1342 gram water.

	Per cent.
Carbon .....	85.07
Hydrogen .....	14.82

Gain in second sulphuric-acid tube 0.0013 gram.

0.1443 gram of a paraffin distillate  $335^{\circ}$ – $343^{\circ}$ , fifty mm., gave 0.4307 gram carbon dioxide and 0.1384 gram water.

	Per cent.
Carbon .....	85.45
Hydrogen .....	14.51

Gain in second sulphuric-acid tube 0.0013 gram.

0.1423 gram of a paraffin distillate  $255^{\circ}$ – $260^{\circ}$ , fifty mm., gave 0.4441 gram carbon dioxide and 0.1423 gram water.

	Per cent.
Carbon .....	85.09
Hydrogen .....	15.08

Gain in sulphuric-acid tube 0.0016 gram.

0.1363 gram of a California distillate, boiling-point  $139^{\circ}$ – $140^{\circ}$ , gave 0.4309 gram carbon dioxide and 0.1337 gram water.

	Per cent.
Carbon .....	84.96
Hydrogen .....	14.72

Gain in second sulphuric-acid tube 0.0009 gram.

0.1459 gram of a California distillate, boiling-point  $185^{\circ}$ – $189^{\circ}$ , gave 0.4559 gram carbon dioxide and 0.1386 gram water.

	Per cent.
Carbon .....	85.70
Hydrogen .....	14.40

Gain in second sulphuric-acid tube 0.0016 gram.

Unless great care be exercised in the rapidity of the combustion I suspect loss of carbon dioxide, but have not yet attempted

to prove it. It will be seen that these results confirmations of Auchy, Drown, Blair, Dudley, and of ordinary form of potash bulb will not retain at all unless the operation be controlled with the thermometer. Another serious difficulty with us has been the impure granular copper oxide. In blank tests it does not show an increase in weight in both sulphuric-acid tube and potash bulb until it has been heated in oxygen as long as would be in six combustions. But when constant weight remains so.

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## SOME FURTHER APPLICATIONS OF HYDROGEN PEROXIDE TO QUANTITATIVE ANALYSIS

BY PERCY H. WALKER.

Received April 8, 1898.

### SEPARATION OF TITANIUM FROM IRON

THE addition of a large excess of hydrogen peroxide to a solution of a ferric salt does not prevent the precipitation of ferric hydroxide on addition of ammonia in excess. A solution of a titanium salt gives, on treatment with hydrogen peroxide, the well-known yellow solution. This solution, with sufficient hydrogen peroxide and kept cold, remains clear, but is precipitated at once on adding ammonia in excess.

Taking advantage of this fact titanium may be separated from iron by the following method: The cold, slightly acid solution of the mixed sulphates (in all about 150 cc.) is mixed with 100 cc. hydrogen peroxide (about two and one-half per cent) and run slowly from a dropping funnel into a beaker containing 100 cc. hydrogen peroxide and 10 cc. ammonia, stirring constantly. The precipitated ferric hydroxide is filtered at once, washed slightly with cold water, and dried. It is then dissolved from the paper with a mixture of hydrochloric acid and hydrogen peroxide, again treated with an excess of hydrogen peroxide and reprecipitated as above. This is repeated until the ferric hydroxide is determined in the ordinary way.

The filtrates containing the titanium are boiled

causes the titanium hydroxide,  $\text{Ti}(\text{OH})_3$ , to separate out in a form easily filtered. This is washed with hot ammonium nitrate solution, ignited, and weighed as  $\text{TiO}_2$ .

Some titanium dioxide was fused with seven grams potassium bisulphate, cooled, dissolved in about 100 cc. cold water, and mixed with a solution of iron ammonium alum containing about one-tenth gram iron. The separation was then carried out as described above.

Titanium dioxide found by first separation.....	0.0872
Titanium dioxide found by second separation.....	0.0104
Titanium dioxide found by third separation.....	0.0041
<hr/>	
Total found .....	0.1017
Theory ( $\text{TiO}_2$ taken) .....	0.1016
<hr/>	
Difference + 0.0001	

#### SEPARATION OF URANIUM FROM IRON.

The presence of a large excess of hydrogen peroxide prevents the precipitation of uranium by sodium hydroxide, but does not prevent the precipitation of ferric hydroxide. A slightly acid solution containing the mixed salts is mixed with fifty cc. hydrogen peroxide, and run slowly with constant stirring into a large casserole containing a solution of five grams sodium hydroxide in fifty cc. water mixed with fifty cc. hydrogen peroxide. This is then diluted to about 400 cc. with hot water, filtered, and washed with hot water. The filtrate which contains all the uranium is made acid with hydrochloric acid, evaporated to dryness on the water-bath, heated to  $110^\circ \text{C}$ . for one hour to separate any silica (from the reagents and glass), dissolved in hydrochloric acid, filtered, and the uranium precipitated with ammonia, washed with ammonium nitrate and ammonia, finally with water, ignited, and weighed as  $\text{U}_2\text{O}_5$ .

The author used in his experiments a solution containing about equal weights of  $\text{Fe}_2\text{O}_3$  and  $\text{U}_2\text{O}_5$ .

	$\text{U}_2\text{O}_5$ taken.	$\text{U}_2\text{O}_5$ found.	Difference.
(a) .....	0.1129	0.1124	—0.0005
(b) .....	0.1056	0.1064	+0.0008

#### SEPARATION OF ZIRCONIUM FROM URANIUM.

The mixture containing two-tenths to three-tenths gram each

$\text{U}_3\text{O}_8$  and  $\text{ZrO}_2$ , is fused with six to seven grams sodium bisulphate and the melt dissolved in cold water. The solution is mixed with fifty cc. hydrogen peroxide and poured into a casserole containing five grams pure sodium hydroxide dissolved in fifty cc. water and fifty cc. hydrogen peroxide. No precipitate forms at first, but after heating on the water-bath for a half hour the zirconium oxide settles to the bottom of the dish as a very heavy precipitate which is filtered and washed with hot water. The precipitate is easily dissolved by a warm mixture of hydrochloric acid and hydrogen peroxide. This solution is boiled, precipitated with ammonia, washed at first with ammonium nitrate solution, then with water, ignited, and weighed as  $\text{ZrO}_2$ .

Zirconium dioxide taken.	Zirconium dioxide found.	Difference.
0.2150	0.2158	+0.0008

In conclusion the author wishes to state that this work was suggested to him by Prof. Dr. P. Jannasch, of Heidelberg, over a year ago, and much of the work was done in his laboratory, but as the results then obtained were not entirely satisfactory, it was not published at that time.

CHEMICAL LABORATORY, STATE UNIVERSITY OF IOWA,  
 APRIL 4, 1898.

## ON THE DECOMPOSITION OF CONCENTRATED SULPHURIC ACID BY MERCURY AT ORDINARY TEMPERATURES.

BY CHARLES BASKERVILLE AND F. W. MILLER.

Received April 9, 1898.

IN a recent number of this Journal,<sup>1</sup> Mr. J. R. Pitman denied the statement of the authors that concentrated sulphuric acid is decomposed by mercury at the ordinary atmospheric temperature, 20° C. Mr. Pitman leaves himself open to the same criticism that could with justice be urged against us; namely, a failure to report the *strength* of the acid obtained in any other way than that by specific gravity.

As is well known, sulphuric acid (sp. gr. 1.84) may contain either 95.6 or 99.2 per cent.  $\text{H}_2\text{SO}_4$ .<sup>2</sup> The apparatus which we made use of did not permit a determination of the specific gravity more accurately than the second decimal place. Sulphuric acid (sp. gr. 1.839) contains 99.70 per cent.  $\text{H}_2\text{SO}_4$ . The acid used

<sup>1</sup> Vol. 20, 100.

<sup>2</sup> Lunge und Isler: Biedermann's Chemiker-Kalender, 1898, p. 186.



by us in the experiments reported (*vid supra*) contained 99.65 per cent.  $\text{H}_2\text{SO}_4$  by analysis. Acid of that strength placed in an air-tight glass-stoppered bottle with pure mercury gave off, in twenty-four hours, sufficient sulphur dioxide to bleach a very dilute potassium permanganate solution. In several instances after allowing a longer exposure the gas was easily recognized by its odor when the stopper was removed.

Whether or no any reaction occurs depends entirely upon the *strength* of the acid used, as independently noted later by M. Berthelot, who states that "boiled sulphuric acid has a slow action on mercury forming sulphate and giving off sulphurous acid." He also states that the reaction occurs only at the maximum concentration.<sup>1</sup> When our paper was read before the society in Detroit, Dr. E. W. Morley, in the discussion following, stated that he had previously made similar observations but had not published them. In a recent letter from him he stated that when freshly distilled cold sulphuric acid was in contact with mercury, he found it impossible to maintain a vacuum on account of the evolution of from one to two cc. sulphur dioxide per day.

An ordinary hydrometer may indicate acid of 1.84 sp. gr., when in fact it may be of 1.837 sp. gr. or 94.2 per cent. acid, which fact we have observed. We have lately (since the appearance of Mr. Pitman's paper) observed that ninety-five per cent. acid does not seem within a reasonable length of time to react in the cold with mercury. Further we have noticed that during three weeks in this climate ninety-five per cent. acid dropped to 94.2 per cent. by allowing the bottle to remain open a few minutes each day. The content of acid more or less exposed to the moisture of the air while being used in a nitrometer could easily change, the stronger the acid the more rapid the change. Acid of ninety-four per cent. serves very well for desiccation in ordinary gas analysis and has no apparent action upon the mercury; however, the authors insist that concentrated sulphuric acid of 99.5 per cent. strength is decomposed by mercury.

UNIVERSITY OF NORTH CAROLINA.

<sup>1</sup> *Chem. News*, 76, 325; *Compt. rend.*, 125, 20.

# THE RELIABILITY OF THE DISSOCIATION-VALUES DETERMINED BY ELECTRICAL CONDUCTIVITY MEASUREMENTS.<sup>1</sup>

BY ARTHUR A. NOYES.

Received May 25, 1908.

## I. VAN LAAR'S CORRECTION OF THE HEAT OF SOLUTION FORMULA.

THERE has recently appeared<sup>2</sup> an article by van Laar in which he claims with the greatest positiveness that the dissociation-values calculated from the electrical conductivity are incorrect. In order to sustain this view, he brings forward certain "proofs" and offers an hypothesis concerning the cause of the supposed unreliability of the conductivity method. The matter is of so great importance and the view of van Laar is, in my opinion, so completely unjustifiable, that I feel compelled to reply to his arguments, and to present the existing proofs of the contrary idea.

As an evidence of his view, van Laar attempted to show that the heats of solution, calculated thermodynamically from the changes in solubility caused by variations of temperature, agreed much better with the experimental values when the theoretical (Ostwald) dilution-law was used in the calculation, than when the empirical (Rudolphi-van't Hoff) law derived from conductivity values was employed. Unfortunately, however, van Laar has not, it seems to me, derived correctly the relation between the change in solubility and heat of solution in the case of dissociated substances. It is apparent that his equation in the derivation of which the empirical dilution-law was assumed is incorrect, since this furnishes an evidently false result in the limiting case of complete dissociation. The equation to which I refer is as follows :

$$\frac{L}{RT^2} = \frac{3}{3-a} \frac{d \log s}{dT}, \dots\dots\dots (1)$$

in which  $L$  expresses the heat of solution ;  $R$ , the gas constant ;  $T$ , the absolute temperature ;  $a$ , the degree of dissociation ; and  $s$ , the solubility. When  $a = 1$ , this equation becomes

<sup>1</sup> Presented at a meeting of the North Eastern Section of the Society.

<sup>2</sup> *Ztschr. phys. Chem.*, 21, 79.

$$\frac{L}{RT^2} = \frac{3}{2} \frac{d \log s}{dT} \dots\dots\dots (2)$$

For complete dissociation, however, this equation must evidently be quite independent of any dilution-law whatever ; for no change in the degree of dissociation takes place in this case. Also, since in the case of a wholly dissociated di-ionic salt the equilibrium constant  $K$ , which occurs in the general van't Hoff equation,

$$\frac{d \log K}{dT} = \frac{Q}{RT^2},$$

is equal to  $s^2$ , the product of the concentrations of the ions, it follows that

$$\frac{L}{RT^2} = \frac{2 d \log s}{dT} \dots\dots\dots (3)$$

an equation which has already<sup>1</sup> been employed and confirmed. Even the equation derived by van Laar under the assumption of the theoretical dilution-law,

$$\frac{L}{RT^2} = \frac{2}{2-a} \frac{d \log s}{dT} \dots\dots\dots (4)$$

becomes simplified to equation (3) when  $a = 1$ . His two equations (2) and (4) therefore lead to different results in the case where the influence of the dilution-law must disappear. Moreover, even the last equation of van Laar cannot be correct in general, although it fulfils the conditions of the two limiting cases ; for it contains no term which represents the change of the dissociation with the temperature. This is, however, obviously necessary ; for the heat of solution of a partially dissociated substance may be regarded as the sum of two quantities, one of which depends on the heat of solution of the undissociated substance, and the other on its heat of dissociation. This latter amount of heat is, however, determined thermodynamically by the temperature-change of the dissociation-constant, while the former is independent of it. Accordingly the sum, the actual heat of solution, must be a function of the temperature-change of the dissociation-constant.

<sup>1</sup> Nernst : Theoretische Chemie, <sup>2</sup>16.

The original equation of van't Hoff<sup>1</sup>

$$\frac{L}{RT^2} = \frac{d \log is}{dT} = (1 + a) \frac{d \log s}{dT} + \frac{da}{dT} \dots (5)$$

satisfies this theoretical requirement. That of van Laar is an attempted improvement on this. According to him the assumption of van't Hoff<sup>2</sup> and Rudolphi<sup>3</sup> that  $L = W + a Q$ , where  $L$  is the actual (total) heat of solution,  $W$ , the heat of solution of the undissociated substance, and  $Q$ , its heat of dissociation, is not correct; but since in the solution of the quantity  $ds$  there takes place, besides its own change in dissociation, a change in the degree of dissociation of the total quantity  $s$  of the substance

present, by an amount  $\frac{da}{ds} ds$ , it follows that  $Lds = Wds + \left(a + s \frac{da}{ds}\right) Q ds$ , in which the quantity  $\frac{da}{ds}$  is to be obtained from the dilution-law. For the heat of solution,  $L$ , of a gram-molecule, it follows, therefore, according to van Laar, that

$$L = W \left(a + s \frac{da}{ds}\right) Q.$$

This "correction" seems to me, however, to be wholly erroneous and to arise from a misunderstanding of the significance of the heat of solution. The molecular heat of solution is, in a thermodynamical sense, the heat which is absorbed by the dissolving of one molecule of the substance in a solution of *unchangeable* concentration; namely, that corresponding to the equilibrium. Even differential changes of concentration must not occur if the thermodynamical relations are to hold strictly; and if they actually occur, as van Laar assumes, the heat of solution then obtained will differ from the thermodynamical heat by an amount corresponding to the influence of those changes in concentration; that is to say, the dissolving must take place with a simultaneous increase in the volume of the solution by the addition of the solvent, in such a way that the concentration remains constant, just as in the reversible evaporation of a liquid the volume of the vapor must increase continuously.

<sup>1</sup> *Ztschr. phys. Chem.*, 17, 147;  $i = (1 + a)$  for a di-ionic electrolyte.

<sup>2</sup> *Ibid.*, 17, 547.

<sup>3</sup> *Ibid.*, 17, 299.

By these considerations it seems to me that the falsity of van Laar's attempted correction of van't Hoff's equation is made evident. The matter is, however, so important, as well from a general point of view as from the standpoint of this discussion, that it seems proper to present a direct derivation of the van't Hoff equation by means of a cyclical process, and especially so since van't Hoff himself, according to the assertion of van Laar,<sup>1</sup> has acknowledged the validity of the latter's proposed correction.

## 2. DERIVATION OF THE RELATION BETWEEN THE HEAT OF SOLUTION OF DISSOCIATED SUBSTANCES AND THE CHANGE IN THEIR SOLUBILITY WITH THE TEMPERATURE.

In order to derive this relation we will consider a cyclical process to be carried out by means of an osmotic machine. The machine consists, in its original condition, of a cylinder provided with a semipermeable piston, in the bottom of which, below the piston, is one molecule of the solid substance, while above is that amount of the pure solvent in which the solid substance is soluble. The solid substance is moistened with an infinitely small amount of the saturated solution, and the osmotic pressure on the piston is just balanced by a corresponding weight. The machine is placed in a very large heat reservoir at  $T^\circ$ , and the following cyclical process consisting of five parts is carried out :

*Part I.* By an indefinitely small decrease of the weight on the piston the latter is allowed to rise until the solid substance is dissolved. Let the concentration of the resulting saturated solution be expressed by  $s$ .

*Part II.* The piston is fastened and the machine placed in a very large heat reservoir at  $(T + dT)^\circ$ .

*Part III.* The piston is set free after loading it with a weight equal to the osmotic pressure; the weight is then increased by an indefinitely small amount, and the piston allowed to sink until the concentration of the solution has risen from  $s$  to that of the solution saturated at  $T + dT$ ; that is,  $s + ds$ .

*Part IV.* The piston is now allowed to sink still further, until the molecule of the substance has separated out of the solution.

<sup>1</sup> *Ztschr. phys. Chem.*, 17, 547.

*Part V.* Finally the machine is placed in the heat reservoir at  $T^\circ$ .

The cyclical process is now completed and the original condition restored. The Second Law of Energetics gives now the relation which must exist between the work  $dA$  performed on the system and the amount of heat  $Q$  which is transferred from one temperature to the other. This relation is

$$dA = Q \frac{dT}{T}. \dots\dots\dots (6)$$

We will next determine the amount of work performed in the above-described process. The work done in each part consists in a change of volume taking place at a constant pressure, and is therefore equal to the product of these two quantities. According to the *Avogadro-van't Hoff* principle, the osmotic pressure is equal to  $nRT$ , where  $n$  denotes the number of molecules present. As above, the concentration of the solution saturated at  $T^\circ$  is  $s$ , and at  $T + dT^\circ$  is  $s + ds$ . Further, let the number of molecules which is present in the solution of one molecule of the solid substance at  $T^\circ$  be  $i$ , and at  $T + dT^\circ$  be  $i + di$ . Then the following values of the change in volume ( $\Delta v$ ), of the pressure ( $P$ ), and of the work performed ( $A$ ), in the separate parts of the process, are :

$$\text{Part I. } (\Delta v)_I = \frac{1}{s}; \quad P_I = is RT; \quad A_I = -iRT.$$

$$\text{Part II. } (\Delta v)_{II} = 0; \quad A_{II} = 0.$$

$$\text{Part III. } (\Delta v)_{III} = -\frac{1}{s} + \frac{1}{s + ds}; \quad P_{III} = is R(T + dT);$$

$$A_{III} = iRT d \log s.$$

$$\text{Part IV. } (\Delta v)_{IV} = -\frac{1}{s + ds}; \quad P_{IV} =$$

$$(i + di)(s + ds) R(T + dT);$$

$$A_{IV} = iRT + iR dT + RT di.$$

$$\text{Part V. } (\Delta v)_V = 0; \quad A_V = 0.$$

The total work done in the process is, therefore,

$$dA = iR (T d \log is + dT).$$

On the other hand, the amount of heat,  $Q$ , absorbed at the temperature  $T$ , is evidently the sum of the heat of solution  $L$  in the ordinary sense (without work being done) and the external work; that is to say,  $Q = L + iRT$ . If these values of  $dA$  and  $Q$  are substituted in equation (6), the expression of the Second Law, we obtain

$$\frac{L}{RT^2} = \frac{i d \log s}{dT},$$

which is the original van't Hoff equation. Attention may be especially called to the fact that in this cyclical process no opportunity is offered for the introduction of van Laar's correction.

This equation is evidently independent of any dilution-law whatever, and of the number of ions into which the electrolyte is dissociated. If the electrolyte breaks up to an extent  $a$  into  $n$  ions,  $i = 1 + (n - 1)a$ , whence follows:

$$\frac{L}{RT^2} = [1 + (n - 1)a] \frac{d \log s}{dT} + (n - 1) \frac{da}{dT}.$$

Now if the electrolyte follows the dilution-law

$$K = \frac{(as)^\nu}{(1-a)s}$$

where  $\nu$  may have any value, then we obtain, by differentiation,

$$\frac{da}{dT} = \frac{a(1-a)}{\nu - (\nu - 1)a} \frac{d \log K}{dT} - \frac{(\nu - 1)a(1-a)}{\nu - (\nu - 1)a} \frac{d \log s}{dT}.$$

By substitution of this value in equation (6) we obtain

$$\frac{L}{RT^2} = \frac{\nu + (n - \nu)a}{\nu - (\nu - 1)a} \frac{d \log s}{dT} + \frac{(n - 1)a(1-a)}{\nu - (\nu - 1)a} \frac{d \log K}{dT} \dots (7)$$

This equation is rigidly exact and general; in it it is presupposed only that the electrolyte follows some exponential dilution-law of the assumed form.

In the two limiting cases where  $a = 1$ , and  $a = 0$ , the equation becomes simplified to

$$\frac{L}{RT^2} = \frac{n d \log s}{dT}, \text{ and } \frac{L}{RT^2} = \frac{d \log s}{dT},$$

as the theory requires. In general, however, in the calculation of the heat of solution, a knowledge not only of the temperature-

change of the solubility, but also of that of the dissociation-constant, is necessary. The latter change has in the case of most electrolytes been shown to be so small that for practical purposes the last member may ordinarily be neglected without a large error, a simplification which is permissible especially in the case of very weakly and very strongly dissociated electrolytes, for the coefficients of  $d \log K : dT$  disappear when  $\alpha$  approaches zero or unity.

We will now consider two special cases : first, where the electrolyte is di-ionic and follows the theoretical (Ostwald) dilution-law, where it is, for example, a weak acid or base ; and second, where the electrolyte is di-ionic and follows the empirical (van't Hoff) dilution-law, where it is, for example, a salt. In both cases  $n = 2$  ; in the first case  $\nu = 2$ , and in the second  $\nu = \frac{3}{2}$ . By substituting these values in equation (7) and omitting the last member we obtain

$$\frac{L}{RT^2} = \frac{2}{2-a} \frac{d \log s}{dT} \text{ when } \nu = 2, \dots\dots (8)$$

$$\text{and } \frac{L}{RT^2} = \frac{3+a}{3-a} \frac{d \log s}{dT} \text{ when } \nu = \frac{3}{2}. \dots\dots (9)$$

The first formula is identical with that obtained by van Laar ; the second is, however, essentially different from his, which reads

$$\frac{L}{RT^2} = \frac{3}{3-a} \frac{d \log s}{dT}. \dots\dots\dots (10)$$

### 3. COMPARISON OF THE CALCULATED AND THE OBSERVED HEATS OF SOLUTION.

In the following tables the results of the calculation of the heats of solution according to the three formulas (8), (9), and (10), given above, are placed together beside the experimentally found values for the four substances used by van Laar. Only those values in the next to the last column are calculated by me ;<sup>1</sup> the rest are those of van Laar.

<sup>1</sup> These values were obtained from those of van Laar in the preceding column by multiplication by  $\frac{3+a}{3}$ . The values of  $a$  used are those derived by van Laar from conductivity measurements ; namely, for silver acetate, 0.713 ; for silver propionate 0.744 ; for silver isobutyrate, 0.718 ; and for *o*-nitrobenzoic acid, 0.303.



## HEATS OF SOLUTION.

	Ostwald's dilution-law assumed. Calculated by (8).	Van't Hoff's dilution-law assumed. Calculated by (10).	Calculated by (9).	Experi- mentally found.
Silver acetate .....	4369	3688	4562	4613
Silver propionate .....	3789	3148	3928	3980
Silver isobutyrate .....	2715	2289	2836	2860
<i>o</i> -Nitrobenzoic acid .....	7167	6766	7449	7083

From the fact that the values in the first column of numbers, which were obtained with the help of the Ostwald law, agree much more closely with the experimental values than do those of the second column, which were calculated by means of van 't Hoff's dilution-law and the equation of van 't Hoff as corrected by van Laar, van Laar concluded that salts in reality follow Ostwald's dilution-law, and not van 't Hoff's, as is to be inferred from the conductivity ; in other words, the conductivity gives, according to him, incorrect values of the dissociation. Further support of this latter assumption he finds in the fact that in the case of the three salts, even the values calculated with the help of Ostwald's law differ from the experimental ones by several per cent. But I have proved above, as I believe, that the equation of van Laar, in the deduction of which van't Hoff's dilution-law was presupposed, is incorrect, and that the true expression is equation (9). If one is to decide between the two dilution-laws, the values of the first and *third* columns of numbers must, therefore, be compared with those of the fourth. This comparison shows now just the opposite result ; in the case of the three salts, the values deduced from van 't Hoff's law agree almost completely (within 0.8 or 1.3 per cent.) with the actual ones, while those from Ostwald's law deviate by about five per cent. Moreover, it is especially worthy of note that the nitrobenzoic acid, which, like all weak acids, follows Ostwald's law, possesses a heat of solution which is in accord with the assumption of the validity of this law, but which is not consistent with van 't Hoff's law. The results are therefore in perfect agreement with the usual assumptions based on conductivity in regard to the dissociation of the substances in question, and not only is the argument of van Laar refuted, but at the same time a new proof is furnished of the validity of van 't Hoff's dilution-law in the

case of salts, and of the reliability of the dissociation-values determined from conductivity measurements.

#### 4. ELECTRICAL CONDUCTIVITY AND INVERSION-VELOCITY IN MIXTURES OF WATER AND ALCOHOL.

Van Laar finds a further proof of his view in the fact that the rate of inversion of sugar by hydrochloric acid, in mixtures of alcohol and water, is essentially different from that in pure water, although according to Cohen<sup>1</sup> the degree of dissociation of the acid, as determined by its conductivity in the two solvents, is the same. Cohen<sup>2</sup> also considers this fact as leading to the conclusion that "in solutions in mixtures of water and alcohol the electrical conductivity is not an entirely correct measure of the degree of dissociation."

It is remarkable that this conclusion has been drawn by two separate investigators; for it appears to me obviously unjustified. Even if the concentrations of the hydrogen ions are the same, it is by no means to be expected that the rates of inversion in the different solvents would be equal. For, aside from the fact that the catalytic activity of the hydrogen ions is not necessarily constant, it is clear that the concentration of one of the reacting substances, the water, undergoes a change; and it would be indeed remarkable if this change had no influence on the rate of inversion. It is not improbable that the ions of the water play an important part in the hydrolysis of the sugar, and it has been shown by Löwenherz<sup>3</sup> that the addition of alcohol considerably reduces the dissociation of water. It is therefore entirely inadmissible to ascribe to the inversion results such a significance as van Laar and Cohen do.

#### 5. VAN LAAR'S "EXPLANATION OF THE DEVIATIONS FROM OSTWALD'S LAW."

It seems superfluous to discuss the hypothesis of van Laar on the cause of the incorrectness of the dissociation-values derived from the conductivity, since, from what has been said above, no reason exists to doubt their correctness. A remark in regard

<sup>1</sup> *Ztschr. phys. Chem.*, 25, 41.

<sup>2</sup> *Ibid.*, p. 44.

<sup>3</sup> *Ibid.*, 20, 204.

to it may be, however, not without interest. If I correctly understand his hypothesis, its essential feature is that the Joule heat-effect which is continuously produced by the current during the measurement of the conductivity, causes a localized increase of temperature around the ions, as a result of which the dissociation is temporarily changed. Against this hypothesis, however, there exists the following fatal objection: if the dissociation and conductivity are affected by the heat produced by the current, then the observed values of these would depend on the strength of the current employed, which is known not to be the case.

#### 6. EXISTING DETERMINATIONS OF THE DISSOCIATION BY INDEPENDENT METHODS.

In his article, van Laar pays no attention to previously published experiments which bear upon the reliability of the conductivity method of determining dissociation; yet certain investigations have been carried out, the purpose of which was to answer this very question. In the first place may be considered the recent investigations of Jones,<sup>1</sup> Loomis,<sup>2</sup> Abegg,<sup>3</sup> and Raoult,<sup>4</sup> on the lowering of the freezing-point of water by cerium salts. Of these the two salts, potassium chloride and sodium chloride, have been most carefully studied, for the lowerings of freezing-point caused by them have been determined by all four of the mentioned investigators.

In order to show now the extent of the agreement of the values with one another and with the results of the conductivity method, I have brought together in the following table the calculated dissociation-values for the concentrations 0.01 to 0.1 normal. In the calculations from the freezing-point lowerings  $1.85^{\circ}$  was assumed as the molecular lowering of water.<sup>5</sup> The conductivity determinations of Kohlrausch were made use of in calculating the dissociation-values by this method.

<sup>1</sup> *Ztschr. phys. Chem.*, 11, 110, 529; 12, 623.

<sup>2</sup> *Wied. Ann.*, 51, 500; 57, 495.

<sup>3</sup> *Ztschr. phys. Chem.*, 20, 207.

<sup>4</sup> *Compt. rend.*, 124, 885; 125, 751.

<sup>5</sup> Compare Abegg: *Wied. Ann.*, 64, 499.

## DISSOCIATION-VALUES.

Normal concentration.	Potassium chloride.						Sodium chloride.					
	Jones.	Loomis.	Abegg.	Raoult.	Mean.	Kohlrausch.	Jones.	Loomis.	Abegg.	Raoult.	Mean.	Kohlrausch.
0.01	95	95	96	..	95.3	94.4	95	99	105	.	99.7	93.7
0.03	92	90	90	91	90.8	91.1	92	93	92	97	93.5	89.6
0.05	90	89	88	88	88.8	89.1	90	91	92	93	91.5	87.3
0.10	87	86	..	85	86.0	86.2	88	88	88	89	88.2	84.2

It is seen that, in the case of potassium chloride, the four separate values by the freezing-point method agree well with one another, and the averages of them are almost identical with the dissociation-values calculated from Kohlrausch's conductivity measurements. In the case of sodium chloride, however, the agreement between the freezing-point results of the separate observers is not so complete, and their averages are about four per cent. higher than the values to which the conductivity leads. Whether this latter result arises from a constant error in the freezing-point determinations or from a theoretical inaccuracy in one of the two methods, can not, of course, be determined at present. In view of this fact it must be admitted, to be sure, that these freezing-point measurements do not contribute much towards answering the question regarding the reliability of the conductivity method. Nevertheless a certain significance is to be attributed to the close agreement in the case of the potassium chloride, the best investigated salt.

In another way, however, more decisive evidence of the reliability of that method has been furnished. From the phenomenon of solubility effect it is possible to determine dissociation-values, and experiments of Noyes and Abbot<sup>1</sup> have shown that the values so determined in the case of certain thallium salts are in accordance with those derived from the conductivity. For details reference is made to the original article; but the final results may be presented here. The first two columns of figures in the following table show the dissociation-values which were calculated from independent solubility experiments with two pairs of salts. The last column contains the corresponding dissociation-values, which were derived from the conductivity.

<sup>1</sup> *Ztschr. phys. Chem.*, 16, 136.

Salt.	From solubility experi- ments. I.	From solubility experi- ments. II.	From the conductivity.
TlCl .....	86.5	86.5	86.6
TlSCN .....	86.7	86.6	85.6
TlBrO <sub>3</sub> .....	89.9	91.9	89.0

These entirely distinct methods, freezing-point-lowering and solubility-effect, lead therefore to nearly the same dissociation-values. That the electrical conductivity furnishes essentially correct dissociation-values in the case of di-ionic salts in moderately dilute solution, is therefore probable. At any rate, more weighty reasons than those brought forward by van Laar must be discovered before this method should be discredited.

## THE ERROR IN CARBON DETERMINATIONS MADE WITH THE USE OF WEIGHED POTASH BULBS.

BY GEORGE AUCHY.

Received June 2, 1898.

THE difficulty, or impossibility even, of obtaining good carbon results in damp weather has been so often spoken of that anything further on the same subject would seem superfluous. Nevertheless the writer ventures a few remarks. In determining carbon by the dry combustion method it was found that, after the prolong had been in use a few times, a loss of moisture occurred as shown by the gain in weight of a potash bulb containing strong sulphuric acid, placed after the prolong. But it was later discovered that this loss was mainly due to the fact of the copper oxide in the preheating furnace being too fine and packed in too tightly. With coarser copper oxide, and a consequently easier passage of gas and air, and therefore less force and speed in aspiration, the amount of moisture lost from the prolong was much lessened, and the increase in the loss very steady and gradual so that a determination of it by means of a sulphuric acid bulb<sup>1</sup> would only be necessary once in a while, and might be altogether dispensed with by a frequent change in the calcium chloride of the prolong. This agrees with Dr. Drown's experience who found by many trials that the prolong retained all the moisture passing into it from the potash bulbs; but, while still using the sulphuric acid bulb, some gains in its

<sup>1</sup> Or better, a small calcium-chloride tube, as it exposes less surface for the condensation of moisture on a damp day.

weight far in excess of that due to the moisture escaping from the prolong occurred. These were followed in one or two determinations afterward by losses of weight sufficiently large to make the weight of the bulb a minus quantity. This gain in weight could only be attributed to an unusual condensation of moisture on the outside surface of the bulbs, and the loss in weight to a return to normal conditions in this respect. The idea was suggested that the sulphuric bulbs might be made useful in measuring and determining the amount of moisture condensing on the potash bulbs; that is, the amount of moisture condensing on the sulphuric bulbs, found by subtracting the amount of inside moisture gained from the prolong if any, from the total gain in weight of the bulbs, might be taken to be the amount of moisture also condensing on the potash bulbs, and the necessary correction in the weight of the latter could then easily be made. But C. B. Dudley somewhere refers to a method of overcoming this difficulty of moisture condensation suggested by Andrew A. Blair which seemed much easier; this was to have an empty potash bulb on the opposite pan of the balance when weighing. This method of Blair's was accordingly tried, retaining, however, the sulphuric acid bulbs as a check. A succession of damp days gave abundant opportunity, and it was found that the unusual gains and losses in the weight of the sulphuric-acid bulbs still continued to occur. But the empty potash bulbs were not of the same type as those to be weighed as directed by Blair. The potash bulbs were of the Geissler form and the empty bulbs of the Liebig form, for convenience in weighing, since the latter shape leaves the pan entirely empty for the weights. As the total surface area of the two bulbs was about the same, the difference in shape was thought to be of no consequence, but from the results it seemed that, either this difference in shape caused a difference in moisture condensation; or the passage of gas, air, and moisture, through the potash and sulphuric bulbs, caused a slight heat which gave a different condensation from that on the empty bulbs; or, the condensation of moisture occurred without rule and uniformity; that is, might occur on the one set of bulbs without occurring also at the same time on the others or not to the same degree and *vice versa*. Tests made by simply

allowing all three of the bulbs stand instead of passing gas and air through two of them as in a determination seemed to show the latter of these theories to be correct. The condensation seems at times to take place entirely at random, so to speak. A condensation on the one bulb does not necessarily mean a condensation on the others, and neither the empty bulbs on the opposite pan nor the weighed sulphuric-acid bulbs are therefore to be depended upon as a means of counteracting, or estimating the moisture condensing on the potash bulbs. The results were as follows :

Time of standing. Hours.	Gain or loss of weight in terms of carbon.	
	Potash bulbs. Per cent.	Sulphuric bulbs. Per cent.
I	—0.007	—0.014
I2	—0.008	—0.007
I	—0.008	—0.006
I2	—0.004	—0.001
I2	0.012	0.012
I2	0.039	0.018
I2	—0.014	—0.005
I2	0.004	0.004
I2	0.002	0.005
I	0.000	—0.002
I2	0.011	0.010
I	0.004	0.007
I2	0.008	0.006
I2	0.005	—0.008
I	—0.013	—0.001
I2	0.003	0.014
I2	0.026	0.027
I	0.006	—0.024
I2	—0.032	—0.026
I2	—0.012	0.010
I	—0.004	—0.006
I2	—0.006	0.007
I2	—0.013	—0.006
I	—0.007	0.004
I2	—0.008	—0.003
I	0.006	0.015
I	0.000	0.000
I2	—0.023	0.008
I	0.032	0.026
I	—0.012	—0.004
I2	—0.006	0.007
I	—0.012	—0.010
I2	0.015	0.029
I	—0.009	—0.010

In taking these weights the empty bulbs on the opposite pan of the balance were used.

Provided the sulphuric bulbs be used to estimate the outside condensation of moisture, and empty bulbs on the opposite pan be also used, what is the error from moisture condensation in a determination? To gain some idea the following tests were made. The first column of results gives the results as they were obtained without any correction for moisture condensation and the very great source of error brought into the process by the use of these sulphuric bulbs, if their gain in weight be always attributed solely to inside moisture from the prolong, is seen by the results of this column. The second column gives the results after being corrected for moisture condensation by the indication of the sulphuric-acid bulbs, assuming the moisture condensing on the potash bulbs to be just equal to that on the sulphuric bulbs. The empty bulbs on the opposite pan were also used.

No.	Apparent result. Per cent.	Corrected result as indicated by sulphuric bulbs. Per cent.	True re- sult ob- tained in dry weather. Per cent.	Error. Per cent.	Moisture condensed on sul- phuric bulbs in terms of carbon. Per cent.	Moisture condensed on potash bulbs in terms of carbon. Per cent.
237	0.976	0.904	0.904	0.000	0.036	0.036
237	0.827	0.927	0.904	0.023	—0.050	—0.027
264	0.024	0.032	0.031	0.001	—0.005	—0.002
278	0.953	0.993	0.983	0.010	—0.020	—0.010
278	1.075	0.975	0.983	0.008	0.050	0.027
1.05	1.096	1.09	1.056 <sup>1</sup>	0.034	0.000	0.039
1.05	1.106	1.104	1.056	0.048	0.000	0.048
1.05	1.15	1.033	1.056	0.023	0.058	0.035
1.05	1.077	1.057	1.056	0.001	0.010	0.010
1.00	0.94	1.06	1.00	0.060	—0.062	0.002
0.625	0.641	0.631	0.625	0.006	0.005	0.011
Dummy	0.024	0.016	0.005	—0.021	0.020	—0.003
"	0.111	0.015	0.005	—0.010	0.048	0.058
"	—0.034	0.036	0.005	0.031	0.035	0.004
"	0.038	0.018	0.005	0.013	0.020	0.023
"	—0.032	0.024	0.005	0.019	0.028	0.009
"	—0.011	0.011	0.001	0.010	—0.011	0.000
Bi	1.125	1.095	1.10	0.005	0.016	0.010
238	0.824	0.935	0.905	0.029	—0.055	—0.025

In the following the "true" result was found by taking the averages of the corrected results:

<sup>1</sup> Booth, Garrett, and Blair's result, 1.053. Result by wet method, 1.063. By dry method, 1.05. Average, 1.056.



No.	Apparent result. Per cent.	Corrected result as indicated by sulphuric bulbs. Per cent.	True re- sult ob- tained in dry weather. Per cent.	Error. Per cent.	Moisture condensed on sulphuric bulbs in terms of carbon. Per cent.	Moisture condensed on potash bulbs in terms of carbon. Per cent.
284	0.272	0.152	0.163	0.011	0.064	0.045
284	0.117	0.177	0.163	0.014	—0.030	—0.016
301	0.18	0.14	0.118	0.022	0.020	0.040
301	0.095	0.137	0.118	0.019	—0.020	—0.003
301	0.119	0.105	0.118	0.013	0.007	—0.006
301	0.134	0.09	0.118	0.028	0.022	0.006
314	0.705	0.805	0.775	0.030	—0.050	—0.020
314	0.89	0.75	0.775	0.025	0.070	0.045
295	0.045	0.095	0.087	0.008	—0.025	—0.017
295	0.135	0.090	0.087	0.003	—0.023	—0.025
295	0.115	0.055	0.087	0.032	0.030	—0.001
295	0.092	0.077	0.087	0.010	0.007	—0.003

The greatest error is 0.06 per cent. though in most of the tests it does not exceed 0.03 per cent., which, in high carbon steels at least, is for ordinary purposes permissible. But 0.06 per cent. is, of course, too great an error. How may it be reduced to within reasonable limits? Probably by using smaller bulbs as is the custom of Dudley; or probably by using small soda-lime tubes as does Stillman, who in his book, "Engineering Chemistry," says that "they are much more convenient and less liable to variation in weight."

The error is, of course, completely eliminated in such methods as that of the Pittsburgh Testing Laboratory described by Handy in this Journal, in which barium hydroxide is the absorbent; the barium carbonate is filtered off, and the excess of hydroxide titrated with standard acid, or, where the carbon dioxide is measured, with corrections for pressure, etc.

In the method described in this article, the question arises, why trouble to use the sulphuric bulbs and the empty bulbs in the opposite pan of the balance, if the condensation of moisture is not at the same occasion equal, nor nearly so in many cases, on all the bulbs used?

The following comparisons of errors were made. These figures are not the results but the errors only. For results (but of the sulphuric bulb column only) see the preceding table:

No. of deter- mination.	Error, using sulphuric bulbs. Per cent.	Error, only potash bulbs used. Per cent.
237	0.000	0.036
237	0.023	0.027
264	0.001	0.002
278	0.010	0.010
278	0.008	0.027
D	0.021	0.003
D	0.010	0.058
D	0.031	0.004
D	0.013	0.023
D	0.019	0.009
D	0.010	0.000
Bi	0.005	0.010
238	0.029	0.025
284	0.011	0.045
284	0.014	0.016
1.05	0.034	0.039
1.05	0.048	0.049
1.05	0.023	0.035
1.00	0.060	0.003
0.625	0.006	0.011
301	0.022	0.040
301	0.019	0.003
301	0.013	0.006
301	0.028	0.006
314	0.030	0.020
314	0.025	0.045
295	0.008	0.017
295	0.008	0.025
295	0.032	0.001
295	0.010	0.003
1.05	0.001	0.010

There is no marked difference in favor of the results obtained by use of sulphuric bulbs. But in actual work, the errors on that side would in many cases be not so extreme, as here indicated, as the operator could average. For instance, in the extreme case "1.00," the error is 0.060 per cent., the condensation of moisture on the sulphuric bulb amounting to —0.062 per cent. Now the operator could not, of course, tell whether the condensation on the potash bulb was also —0.062 per cent. or nothing at all, or somewhere between. If it also occurs to that amount on the potash bulbs, then the true result is 1.06 per cent. If it does not occur at all on the potash bulbs then

the result is 1.00 per cent. By averaging he would get a result of 1.03 per cent. which would not be more than 0.03 per cent. away from the truth in either case, and might be much closer than that, so that in this way it is sometimes advantageous to use the sulphuric bulbs, but whether this advantage is sufficient to compensate for the double labor of weighing two bulbs is perhaps doubtful. In cases where the condensation is on the potash bulbs only as in "1.05", of the first table, and none happens on the sulphuric bulbs, there of course the latter are of no use whatever and the whole error falls on the result as much so as if they had not been used; also if the moisture condensation is confined to the sulphuric bulbs, they are of no avail except to introduce an error into the result, not more than 0.030 per cent. however, although the table shows this to be of infrequent occurrence, both bulbs being usually affected, though rarely to the same degree. As before said, the true remedy is doubtless in the use of smaller bulbs, or in the substitution of soda-lime tubes.

In getting the dummy result it is obviously better to use a small calcium-chloride tube than the potash bulbs; as the dummy result, if any, is simply due, if a preheating furnace be used, to moisture escaping absorption by the drying train, no potash need be used; and also in determining the moisture escaping the prolong, it is better to use the small calcium-chloride tube, making several tests. The dummy results in the table show the impossibility of getting anything like absolute blanks, or anything like true blanks by the usual method in very damp weather.

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## THE CHEMISTRY OF CASCARA SAGRADA.<sup>1</sup>

BY ALFRED R. L. DOHME AND HERMANN ENGELHARDT.

Received May 27, 1898.

THE most generally used medicines are most probably laxative medicines, and the most generally used laxative medicine is most probably cascara sagrada bark. This is due to the remarkable property it possesses of being a tonic as well as a laxative, and in no less degree to the fact that its action is

<sup>1</sup> Presented by the Special Research Committee at the Forty-Fifth Annual Meeting of the American Pharmaceutical Association, August, 1897.

sure and comparatively free from any accompanying unpleasant effects. Most persons can use it regularly for years without it losing its virtues for their particular case. No drug in the pharmacist's armamentarium has sprung into such sudden prominence and has increased in general use to such extent as cascara sagrada. Even conservative Europe, and especially conservative pharmaceutical Europe, has opened its arms and welcomed the "sacred bark" of the Pacific coast as a worthy companion of or possible successor to senna, aloes, or rhubarb. The history of cascara sagrada has been told by Prof. J. U. Lloyd to this association last year at Montreal, and we will not enter upon it here. Quite a number of publications upon the drug and its sister drug, buckthorn bark, have been sent us by the Chairman of the Special Committee of Research of the American Pharmaceutical Association, and we wish to express to him our thanks for the willingness with which he undertook to procure us copies of the various literature we needed for the work. Inasmuch as most of these publications and articles were upon the active principle of the drug and methods of isolating it, and most of them obtained varying results and different compounds, and none of them gave a complete analysis of the drug, we concluded to apply to cascara sagrada the systematic method of plant analysis suggested by Parsons and given in his book upon plant analysis, as well as in Prescott's "Organic Analysis." The result of this proximate analysis of cascara sagrada we will hence give first, giving the detail of the work on the glucoside afterwards.

The cascara sagrada bark used in the investigation was a typical specimen with a light gray cork layer on the outside and a yellowish brown cortical parenchyma layer on the inside. It was gathered in Oregon, and was somewhat less than one year old. It was in thin quills, and markedly bitter when chewed for a few minutes. It was powdered to a number eighty powder and then possessed in that form a yellowish brown color. In cross-section under the microscope it appeared as given in the accompanying sketch.

#### I. DETERMINATION OF MOISTURE.

Weighed quantities of the air-dried powder were carefully heated in an air-bath at  $110^{\circ}$  C. to constant weight, and as the

mean of six determinations we found that it contained 8.3 per cent. of moisture. Its color was not perceptibly altered by the repeated heating at this temperature.

#### CROSS-SECTION OF CASCARA SAGRADA BARK.

*x*, 100 diam., *Δ*, cork cells; *cp*, cortical parenchyma, *r*, stone cells; *δ*, bast fibers; *mr*, medullary rays; *l*, libriform.

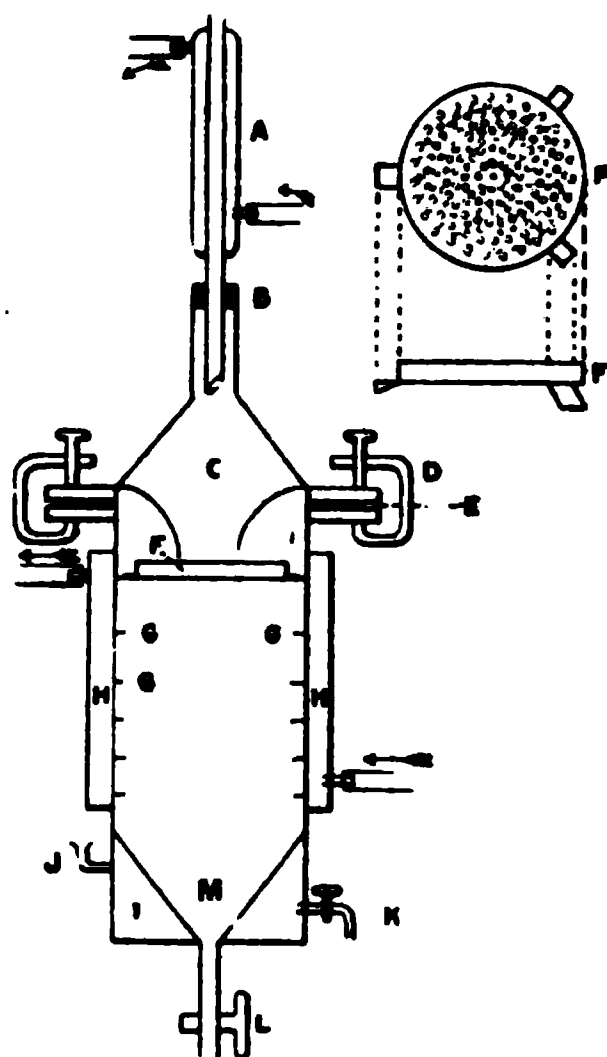
#### II. DETERMINATION OF ASH.

Weighed quantities of the air-dried powder were carefully incinerated in a platinum dish and finally heated to a bright red heat over a Bunsen burner to constant weight. As the mean of five determinations, the ash was found to represent seven per cent. of the drug, the analysis varying between 6.9 and 7.05 per cent. as extremes. The bark is very difficult to incinerate, as it carbonizes very easily and then cakes, requiring repeated turning and long-continued heating to finally get it all reduced to a uniform gray color. A qualitative analysis of the ash showed the presence of sodium, potassium, and aluminum, with traces of calcium and iron, together with silicic acid and traces of hydrochloric and sulphuric acids.

#### III. CHLOROFORM EXTRACT.

Although Parsons recommends the use of kerosene to extract

the oils, wax, fat, etc., we found that chloroform answered fully as well. The drug was extracted for five hours in a specially devised apparatus which we constructed, and which is especially adapted to the extraction of large quantities of drug, and is more expeditious than the Soxhlet or Flückiger apparatus. The apparatus is given below.



DRUG EXTRACTION APPARATUS.

*A* is a Liebig's condenser; *B* is a cork stopper closing head of apparatus *C* and connecting the condenser with it; *C* is the head of the apparatus, which is round like a still and attached to the body of the same by a series of clamps *D* joined by asbestos *E*; *F* are perforated tin plates containing drug and resting upon holders *G* on the inside of the apparatus; *H* is a jacket around the apparatus into which cold, warm, or hot water can be let as wanted; *I* is a similar jacket for bottom of apparatus with inlet *J* and outlet *K*; *L* is the stop-cock of the apparatus; *M* is a funnel-shaped termination of the body of the apparatus, itself terminating in the stop-cocked tube *L*; *P* is a cross-section of one of the perforated plates which have a round piece of filter-paper over all the perforations, and the drug then placed on this.

*To operate* the apparatus, which is air-tight, charge all the plates, or as many as are needed, with the powdered drug. Pour the menstruum into the apparatus through the condenser tube of *A*, until enough has been added to saturate all the drug and to fill the funnel *M* half full. Then apply a Bunsen burner to the jacket *I*, thus causing the menstruum here to evaporate and pass up through the apparatus and be condensed in *A* and drop

back into the apparatus. If it is a volatile menstruum, the jacket *H* can be supplied with cold water to aid in its condensation; but if, on the other hand, the menstruum is vaporized with difficulty, warm or hot water can be passed into the jacket *H* to facilitate the volatilization of the same and prevent its recondensation before reaching the condenser *A*. After heating the jacket *I*, and continuing the extraction for half an hour or more, pass cold water into the jacket *I*, when all the menstruum in the apparatus will be drawn down into the funnel *M*, whence it can be drawn by the stop-cock *L*. Fresh menstruum is then added as before, and the process repeated until the extract drawn from the stop-cock is colorless.

#### VOLATILE OIL.

The result of the extraction with chloroform was a dark greenish brown oil of a pronounced odor, reminding strongly of the drug. The yield was 7.5 per cent. of the air-dried drug. We supposed from the pronounced odor that a volatile oil was contained in this extract, and were not mistaken in our conjecture, as we found upon treating the extract with steam that a yellowish green oil passed over with some of the chloroform. This oil was separated from the chloroform, in which it is soluble with very great difficulty, and after redistillation in a vacuum was obtained comparatively pure, but in very small quantity. It is extremely volatile, and possesses, to a marked degree, the characteristic odor of cascara sagrada bark, which hence in all probability derives its odor therefrom. Too little of it was obtained for an analysis, and efforts to saponify it proved fruitless on account of its volatility and the fact that when treated in a sealed tube with saponifying agents it was completely resinified.

#### FIXED OIL.

The oil remaining in the distilling flask after all the volatile products had been driven off by steam, was again heated with water, and the latter drawn off and tested for alkaloids with potassium mercuric iodide. As no precipitate was obtained, no alkaloids were extracted by the chloroform. Treatment of the aqueous solution with basic lead acetate gave no precipitate,

showing absence of glucosides. It was then warmed slightly with dilute sulphuric acid to recover possibly present free alkaloïds, but the effort resulted negatively also. It was then boiled with caustic potash to saponify the fixed oil, and after a short while it was entirely dissolved. After cooling, the solution was extracted with ether which left on evaporation a colorless oil. This oil soon became solid upon standing. It was recrystallized from alcohol and thus obtained in white leaflets melting at  $24^{\circ}$ – $26^{\circ}$  C. An analysis by combustion with copper oxide in a stream of oxygen, by the open tube method, gave the following results :

I. 0.107 gram substance gave 0.3024 gram  $\text{CO}_2$  and 0.172 gram  $\text{H}_2\text{O}$ .

II. 0.1315 gram substance gave 0.3715 gram  $\text{CO}_2$  and 0.210 gram  $\text{H}_2\text{O}$ .

Calculated for $\text{C}_{12}\text{H}_{26}\text{O}$ . Per cent.	I. Per cent.	Found. II. Per cent.
C = 77.42	C = 77.07	C = 77.2
H = 13.98	H = 14.4	H = 14.5

The substance is hence one of the numerous possible isomeric dodecyl alcohols, probably the normal dodecyl alcohol which melts at  $24^{\circ}$  C. It was found to be quite a difficult matter to separate and obtain pure the two fatty acids which are combined with the above dodecyl alcohol to make up the fixed oil of cascara sagrada. However, we believe our results hardly leave any doubt as to their identity. To obtain them, the alkaline liquid, which has been extracted with ether to obtain the above alcohol, was heated to remove all the ether and then treated with hydrochloric acid, which precipitated an oil. This oil soon became solid and was then found to melt at  $30^{\circ}$  C., although all efforts to purify it by crystallization from alcohol proved futile. The potassium salts of the acids were hence prepared by dissolving the substance in caustic potash and then purified by fractional crystallization from alcohol. As obtained therefrom, it crystallized in pearly leaflets and the acid obtained from it melted at  $57^{\circ}$  C. An analysis of the acid potassium salt showed it to be a mixture of stearic and palmitic acids. The neutral potassium salt was of course obtained when the fatty oil was saponified by means of caustic potash, but on treating this



with alcohol or water it was converted into the acid salt. The analyses follow :

0.211 gram substance was incinerated and heated to constant weight with sulphuric acid and gave 0.032 gram  $K_2SO_4$ .

0.178 gram, similarly treated, yielded 0.027 gram  $K_2SO_4$ .

	Per cent.	Found.	
		I. Per cent.	II. Per cent.
Calculated for acid potassium palmitate..	K = 7.09	.....	.....
"      "      "      "      stearate ...	K = 6.43	K = 6.8	K = 6.9

The analyses would indicate that the salt obtained was most likely acid potassium palmitate, but the melting-point of the free acid at  $57^{\circ} C.$ , which is below that of palmitic acid,  $69.2^{\circ} C.$ , and that of stearic acid,  $62^{\circ} C.$ , indicates that it is very likely a mixture of both, as a mixture of several substances nearly always tends to lower the melting-point of either. The conclusion reached is then that the fixed oil of cascara sagrada is a mixture of dodecyl palmitate and dodecyl stearate, and we regret that we were unable to definitely settle this point, and hope to be able to do so during the course of the coming autumn.

#### IV. EXTRACT WITH EIGHTY PER CENT. ALCOHOL.

The residue from the chloroform extract, which had assumed a slightly darker color after being dried, was extracted for twelve hours with eighty per cent. alcohol. The menstruum extracted twenty-seven per cent. of the original air-dried powder. After distilling off the alcohol, there remained a brown, rather hard residue, possessing the characteristic bitter taste of cascara sagrada. It was boiled for half an hour with absolute alcohol, which dissolved the greater portion of it. The solution obtained in absolute alcohol was heated until all the alcohol had passed off, and then extracted with warm water and the aqueous solution treated with basic lead acetate. The result was a reddish brown precipitate, which we believe consisted of a mixture of the lead salt of the glucoside with the lead salts of the tannates present, inasmuch as the precipitate formed by treating the pure glucoside with the same reagent is brick-red in color. It was filtered off and stirred up with water while hydrogen sulphide was passed through to remove all the lead. The lead sulphide was filtered off and the filtrate evaporated to dryness,

resulting in a brown amorphous residue which is soluble in alcohol, acetone, and ethyl acetate. Recrystallized from any of these it forms fine, dark brown needles, but only in small quantities, the majority separating out again in an amorphous condition. This is the glucoside of cascara sagrada which we have named purshianin, analogously to the glucoside frangulin obtained from *Rhamnus frangula*. That portion of the residue from the eighty per cent. alcohol extract found to be insoluble in absolute alcohol, was treated with hot water and the resulting solution treated similarly with basic lead acetate. The result was a dirty yellow precipitate which, after removal of the lead, gave a dark brown resinous substance, different in color from that obtained from the portion soluble in absolute alcohol. We will enter into the details of the work on these glucosides later.

#### V. HOT WATER EXTRACT.

The residue from the absolute alcohol extraction, which had now assumed a dark brown color and was practically devoid of taste, was macerated for twelve hours with water and then filtered. The aqueous extract was evaporated to dryness and found to represent about 12.3 per cent. of the weight of the original air-dried drug. It had a dark brown color and was devoid of any taste. The residue from this aqueous extract was boiled with dilute sulphuric acid (1 : 100) to invert all starches present, and the residue filtered off and dried. The amount of starches, sugar, etc., so extracted was not determined, but will appear in the final résumé of the analysis as difference after everything else has been determined.

#### VI. DILUTE ALKALI EXTRACT.

The dried residue from the hot water extraction was treated with a half per cent. caustic potash solution, which extracted 21.3 per cent. of the original powder, including most all of the remaining coloring-matter. The residue from this extraction was treated with calcium hypochlorite to bleach it, and then yielded 16.1 per cent. of practically white cellulose.

Summed up, these analyses show that cascara sagrada is made up as follows :

	Per cent.
I. Moisture .....	8.3
II. Soluble in chloroform .....	7.5
III. Soluble in eighty per cent. alcohol.....	27.5
IV. Soluble in hot water.....	12.3
V. Soluble in dilute alkali.....	21.3
VI. Cellulose .....	16.1
VII. By difference, starch, etc.....	7.0
	<hr/> 100.0

#### THE GLUCOSIDES OF CASCARA SAGRADA.

We next desire to speak in detail of the work we have done upon the glucosides of cascara sagrada. The literature on the glucosides of buckthorn and cascara sagrada is quite extensive, and we will give a general account of what has been done upon them by other investigators. Buckthorn bark (*Rhamnus frangula*) had been investigated quite considerably before cascara sagrada was known and studied. Casselmann,<sup>1</sup> and later Enz,<sup>2</sup> worked on buckthorn bark and obtained therefrom citron-yellow silky crystals, which were tasteless and odorless, and melted at 226° C. Their composition was for a long time a matter of dispute among chemists, Hesse<sup>3</sup> claiming that the formula was  $C_{10}H_{10}O_{10}$ , which was also verified by Faust; but Casselmann set up the formula  $C_6H_6O_6$  as the result of his analyses. Faust then decomposed the substance by treating it with alcoholic hydrochloric acid and discovered that it was a glucoside, as it yielded him sugar and an acid which he named frangulinic acid. This he obtained in golden yellow crystals, melting at 248°–250° C., difficultly soluble in water, chloroform, and benzene, but easily soluble in ether and alcohol, as well as in alkalies, in which latter it dissolved with formation of a purple-red color. Later investigations showed that this frangulinic acid was the same as emodin, which is trioxymethylanthraquinone. According to Baeumker<sup>4</sup> it is quite an active laxative. Thorpe and Robinson<sup>5</sup> and Thorpe and Miller<sup>6</sup> went into the matter more closely and

<sup>1</sup> Casselmann : Ann. Chem. (Liebig), 104, 77.

<sup>2</sup> Enz : Vierteljahr. d. prakt. Pharm., 16, 106.

<sup>3</sup> Hesse : Ann. Chem. (Liebig), 117, 349.

<sup>4</sup> Baeumker : Exper. Beitr. zur Kenntniss der pharm. Wirkung von Frangulasäure, Göttingen, 1880.

<sup>5</sup> Thorpe and Robinson : J. Chem. Soc., 57, 38.

<sup>6</sup> Thorpe and Miller : *Ibid*, 61, 1. .

determined that the glucoside had the formula  $C_{11}H_{10}O_6$ , and was split up by acids into emodin and a dextrorotatory sugar, which is not glucose, however, but was identified by them as Rhamnose. Schwabe's<sup>1</sup> work on cascara sagrada is quite extensive, and he concluded that the active principle is emodin, which melts at  $254^{\circ}$  C., and whose formula he determined to be  $C_{11}H_{10}O_6 + H_2O$ . The cascarin of Le Prince<sup>2</sup> is certainly not a pure substance, to judge by the description given.

Summed up, the work done indicates that buckthorn bark contains a glucoside frangulin and that this is split up into emodin, which is trioxymethylanthraquinone, and a sugar, Rhamnose or isodulcite, and further, that cascara sagrada contains emodin but not frangulin. We proceeded as follows in obtaining the glucoside of cascara sagrada which had, up to the time of our work, not been obtained. The drug was extracted with chloroform to remove fats, etc., and the residue extracted with eighty per cent. alcohol, and the resulting extract dried and dissolved in hot water. On cooling, some resinous, waxy substance separated and was filtered off. The filtrate was treated with lead acetate, which produced a yellow precipitate. This was filtered off and stirred with hot water on a water-bath. As the lead tannates are difficultly decomposable by hydrogen sulphide it is advisable to pass this gas through the suspended precipitate of lead salts at a temperature of about  $100^{\circ}$  C. This was done until on shaking the flask, whose mouth was closed by the thumb, the latter was raised by the pressure of the gas. The lead sulphide was filtered off and the filtrate evaporated to dryness, resulting in a dark brown substance which consisted mainly of tannins, as portions of them dissolved in water gave good inks on treatment with ferric salts. This tannate mass appears to be composed of several tannins which we did not undertake to investigate, reserving that for a later time, should Prof. Trimble not find time to undertake the same. The filtrate from the lead tannin was treated with basic lead acetate and gave a dark red-brown precipitate of lead glucosides. It is not by any means pure, or it would be colored more nearly cinnabar-red. The precipitate is stirred with hot water in a flask and treated with hydrogen

<sup>1</sup> Schwabe : *Archiv. d. Pharm.*, 226, 569.

<sup>2</sup> Le Prince : *Compt. rend.*, 115, 286.

sulphide as before. The filtrate from the lead sulphide on evaporation yields a hard, brown-red substance which is very difficult to obtain in a crystalline form, as efforts to crystallize it from acetone and ethyl acetate resulted only in our obtaining a few dark brown-red needles melting at  $237^{\circ}$  C., the most of it separating out in an amorphous condition. Not sufficient of it was obtained to make an analysis, but we could confirm that it was not emodin, as it gave no purple color on being treated with caustic potash. It is the glucoside of cascara sagrada which has so far eluded capture, and we have named it purshianin as already explained, being analogous to the frangulin of buckthorn bark. On heating it with alcoholic hydrochloric acid we obtained a sugar and a product which proved to be emodin. The product obtained by heating the purshianin with alcoholic hydrochloric acid was poured into cold water, when a yellow crystalline substance separated out. This was recrystallized from ethyl acetate, which proved the best solvent for the purpose, and separated therefrom in reddish yellow needles melting at  $254^{\circ}$  C. (one lot melted at  $265^{\circ}$  C.) and producing a blood-red color on treatment with caustic alkalies. The crystals were dried at  $110^{\circ}$  C. and appeared to lose some moisture during the process, which was not, however, determined. The analysis of these reddish yellow needles, dried at  $100^{\circ}$  C., resulted as follows:

I. 0.257 gram gave 0.6304 gram carbon dioxide and 0.0972 gram water or 66.9 per cent. carbon and 4.2 per cent. hydrogen.

II. 0.091 gram gave 0.02330 gram carbon dioxide and 0.032 gram water or 66.83 per cent. carbon and 3.9 per cent. hydrogen.

Calculated for  
 $C_{18}H_{10}O_8$ .  
 C = 66.6  
 H = 3.7

Found.	
I.	II.
C = 66.9	C = 66.83
H = 4.2	H = 3.9

These figures, together with the melting-point  $254^{\circ}$  C., leave little doubt but that the substance in hand was emodin, which has also been found to be the active principle of buckthorn bark and likely in a measure of rhubarb. The sugar that is formed when purshianin is saponified appears to be dextrorotatory and non-fermentable, but we have not yet examined it with sufficient care to arrive at a definite conclusion as to what it is. It will

be necessary to obtain a quantity of it, make its osazone, and endeavor to recognize it by the properties and analysis thereof. It appears that the glucoside purshianin is certainly one of the active principles of the drug as in doses of one-fifth of a grain it produces the effects of the drug as far as these affect the bowels. Purshianin is tasteless and odorless, and soluble in alcohol, ethyl acetate, acetone, alkalies, and hot water. We wish to reserve for ourselves its further study, which we hope will bring to light wherein the difference between frangulin and purshianin lies. Frangulin is an orange-yellow powder melting at  $225^{\circ}$  C., according to Thorpe and Robinson, while we find that purshianin is a dark brown-red crystalline substance melting at  $237^{\circ}$  C. Curiously enough, both are glucosides and yield the same substance on being saponified; *viz.*, emodin. The difference cannot hence lie in anything but the sugars that are combined with the emodin to form the glucosides, or perhaps in the way in which these are combined. A fact it is, nevertheless, and notwithstanding the above apparent marked similarity, that cascara sagrada acts more agreeably and effectively than buckthorn bark, which it has practically supplanted. It may be possible that both of these drugs do actually contain as their active principle the identical glucoside, and that the cascara either contains more of it or produces a happier result on the patient by virtue of its other accompanying constituents. We hope to be able to solve this question this autumn, and also to isolate the bitter principle of the bark and determine in what way magnesia or lime removes or alters the same so as to render the preparation free from bitterness.

## LITERATURE UPON RHAMNUS FRANGULA AND RHAMNUS PURSHIANA.

- 1875, Liebermann: *Ber. d. chem. Ges.*, 8, 970; *J. Chem. Soc.*, 29, 251.  
1876, Liebermann and Waldstein: *Ber. d. chem. Ges.*, 9, 1775; *J. Chem. Soc.*, 31, 477.  
1879, Prescott: *Am. J. Pharm.*, 51, 165.  
1885, Kennedy and Wiltrout: *Proc. Am. Pharm. Ass.*, 33, 499.  
Limousin: *J. Pharm. Chim.*, (5), 6, 80; *Pharm. J. Trans.*, 15, 615.  
1885, Wise: *Western Druggist*, 7, 89.  
1886, Wenzell: *Pharm. Rundschau*, 4, 79; *Pharm. J. Trans.*, 16, 918.  
1887, Butterfield: *Pharm. J. Trans.*, 18, 473.  
1888, Meier and Webber: *Am. J. Pharm.*, 60, 87.  
1888, Eccles: *Drug. Circ.*, 32, 54; *Proc. Am. Pharm. Ass.*, 36, 402.

- 1888, Schwabe : *Archiv. Pharm.*, 226, 569; *Proc. Am. Pharm. Ass.*, 37, 491.  
 1889, Findlay : *Pharm. J. Trans.*, 20, 491.  
 1889, Fuge : *Pharm. J. Trans.*, 19, 736.  
 1889, Zeig : *Proc. Am. Pharm. Ass.*, 37, 261.  
 1890, Rusby : *Proc. Am. Pharm. Ass.*, 38, 203; *Bulletin Pharm.*, 5, 115.  
 1892, Blanc : *Revue Therapeutique*, 326.  
 1892, Le Prince : *Compt. Rend.*, 115, 286; *Pharm. J. Trans.*, 23, 183; *Proc. Am. Pharm. Ass.*, 41, 691.  
 1892, Phipson : *Compt. Rend.*, 115, 474; *Repert. d. Pharm.*, October.  
 1893, Braeutigam : *Pharm. Centralh.*, 34, 383.  
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BALTIMORE, AUGUST 1, 1897.

## MOLECULAR WEIGHTS OF SOME CARBON COMPOUNDS; A FEW WORDS MORE.

BY C. L. SPEYERS.

Received May 26, 1898.

IN a short review by Noyes<sup>1</sup> of an article by me,<sup>2</sup> Noyes writes : " No discussion of the results is given, however, nor is any evidence of their accuracy presented, which is particularly unfortunate, since, according to the reviewer's experience, a Beckmann thermometer, which is subjected to considerable variations of pressure, may give quite unreliable readings, owing to the imperfect elasticity of the bulb."

In regard to the discussion of the results, I would state that the measurements made at the boiling-points under ordinary pressures need no discussion; such measurements have been thoroughly discussed by others. In regard to the measurements made under reduced pressure, I would state that I am altogether at a loss to account for the peculiar results obtained. The values given under " cor." in my article show that the rise in the temperature is, in most cases, probably the rise actually caused by the substance dissolved and that the rise is not appreciably influenced by irregular boiling nor by the very slight change in pressure during a set of determinations.

In regard to an error that might seem to come from the imperfect elasticity of the thermometer bulb, I would state that

<sup>1</sup> *Rev. Am. Chem. Research*, 4, 55 (1898).

<sup>2</sup> *J. Phys. Chem.*, 1, 766 (1897).

I had already considered that possibility and came to the conclusion that such an error could not be serious in my measurements. In the first place, I did not introduce any substance until the thermometer was either stationary or changing in such a steady way that the change during the solution could be accounted for and corrected with very few exceptions, which exceptions are readily seen in the high values of their corrections. These high values are due to the long time needed for the solution of the less soluble bodies at low temperatures.

Moreover, the effect of imperfect elasticity in the bulb of the thermometer would seem to be such as to always reduce the rise of the mercury, but in many cases the rise is too great. Besides, in some cases, the measurements of a whole series are very satisfactory.

I do not think that there is any evidence of a disturbance coming from the elasticity of the bulb.

On the other hand, in regard to the imperfect elasticity of thermometer bulb in a series of experiments such as Noyes and Abbot made,<sup>1</sup> it is easy to see that imperfect elasticity of the bulb might prevent the use of a thermometer like that of Beckmann, for in their experiments the thermometer had to show, with great precision and throughout a considerable period of time, a certain constant temperature, and not a variation of temperature throughout a very short time, as it had to do in my case.

Finally I would repeat that my object was to determine the molecular weights of carbon compounds at the ordinary temperatures,  $25^{\circ}$ – $35^{\circ}$ , as I stated in the article reviewed, and not to determine the effect of temperature on the molecular raising, as the reviewer seemed to assume.

RUTGERS COLLEGE, MAY 11, 1898.

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## NOTE ON DROWN'S METHOD OF DETERMINING SILICON IN STEEL.

BY GEORGE AUCHY.

Received May 24, 1898.

**I**N determining silicon in steel by Drown's method there is some reason to believe that sometimes not all the silicon is obtained.

<sup>1</sup> *Ztschr. phys. Chem.*, 23, 56.



Says Dr. Dudley :<sup>1</sup> " Our observations point to the view that the difficulty of insufficient dehydration is due to the separation of iron salts as the sulphuric acid concentrates. These salts enclose gelatinous silica, and prevent the dehydrating acid from getting at it. Unless great pains are taken, therefore, to secure this contact by sufficient stirring, the results will be low."

In this connection it is perhaps worthy of note that if the evaporation be performed with *aqua regia* and sulphuric acid instead of with nitric and sulphuric acids (boiled down rapidly in a porcelain casserole on a very hot plate, and with a watch-glass suspended above casserole by small pieces of bent glass rod), the iron salt is kept in solution till the very last moment when it suddenly crystallizes out and the fumes of sulphuric acid appear, almost at once if the plate be very hot, and very soon afterward if not so hot; and it is therefore a reasonable supposition that this method of procedure is more favorable to a complete dehydration of the silica than the usual nitro-sulphuric process, in which the iron sulphate begins to separate out long before the expulsion of the nitric acid. If the additional precaution be taken to make a second evaporation before filtering, it may in the writer's opinion be confidently expected that no notable amount of silica will escape dehydration. A number of tests were made by evaporating the filtrates, in steels containing about 0.25 per cent. silicon, without getting additional silicon more than 0.005 per cent. which is an amount that may be ignored in ordinary technical work, on steels of that percentage (0.25). A steel which gave 0.122 by one evaporation, gave 0.126 upon repeating the test and making two evaporations before filtering.

4.6667 grams are taken in a porcelain casserole, and treated with fifty cc. of a mixture of 500 cc. of nitric acid (two parts acid to three parts water), 300 cc. of strong sulphuric acid, and 200 cc. of water, equivalent to twenty-five cc. nitric acid (two to three), fifteen cc. strong sulphuric acid, and ten cc. water to a test. When the steel has dissolved, fifteen cc. of strong hydrochloric acid are added, the watch-glass suspended above the casserole by three small bent glass rods, and the liquid boiled down rapidly, using a very hot iron plate.

<sup>1</sup> This Journal, 19, 106.

Very noteworthy is the ease and rapidity with which this evaporation is made. Unlike the nitro-sulphuric acid boiling down, the boiling proceeds very quietly and without any bumping and spattering even at the moment of solidification and after, so that no attention is required.

In high carbon steels the silica is brown from undissolved carbon which, however, upon ignition immediately burns off.

LABORATORY OF THE KEYSTONE SAW WORKS,  
PHILADELPHIA, PA.

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NOTE.

*Preparation of Sodium Benzenesulphonate.*<sup>1</sup>—The directions given by Gattermann in his "Praxis des organischen Chemikers" are usually so accurate that it seems desirable to call attention to a needed alteration in the details of the method for preparing sodium benzenesulphonate (p. 217).

Repeated experiments show that by adding the products of sulphonation, when using fuming sulphuric acid (sp. gr. 1.87), to three or four times the volume of saturated salt solution, as he directs, a sulphonate, containing on an average thirty-seven per cent. of sodium chloride, is obtained.

This contamination may be avoided almost entirely by using four volumes of a less concentrated salt solution. One showing a specific gravity of 1.151 at 18° gives the best results.

The advantage of the modified method is seen from the details of two preparations, in each of which twenty grams of benzene and seventy-five grams of sulphuric acid (sp. gr. 1.87), were used. In No. 1, 240 cc. of a saturated salt solution (sp. gr. 1.204), in No. 2, 254 cc. of a solution (sp. gr. 1.151), were used. The yield of crystals, after filtering through asbestos and drying on a porous plate, was :

No.	Yield in grams.	Composition, in grams.	
		$C_6H_5SO_3Na$ .	NaCl.
1	75	48.1	26.9
2	46	45.6	0.4

With a slight sacrifice in yield a high degree of purity is obtained.

The method outlined by Prof. W. A. Noyes, "Organic

<sup>1</sup> Read before the Cincinnati Section, April 15, 1898.

Chemistry for the Laboratory," p. 84, is less simple, but gives an equally pure product with a loss, however, of about ten per cent. in the yield.

HENRY W. HOCHSTETTER.

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### NOTICE.

The Organization Committee of the Third International Congress of Applied Chemistry requests the American chemists wishing to send contributions to that Congress, either papers or reports of any description, to transmit the full title, together with an abstract of the papers, as soon as possible to Prof. Dr. F. Strohmer, IV/2 Schönburgstrasse Nr. 6, Wien, Austria. It is desired to publish the full program of the papers to be presented in the near future, and the American chemists are earnestly requested to send forward their contributions without delay.

H. W. WILEY,

*Chairman American Committee.*

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### NEW BOOKS.

ANIMAL FATS AND OILS. By LOUIS EDGAR ANDRÉS. Translated by CHARLES SALTER. New York: D. Van Nostrand Co. 1898. xii + 240 pp. Price \$4.00.

This volume deals with the technology of animal fats and oils, and is a valuable work, not only for the student, but also for the practical manufacturer of oil and fat products. The first few pages, which are devoted to the occurrence, origin, properties, and chemical constitution of animal fats, deal briefly with the raw materials from which commercial fats and oils are derived, and review the chemical structure of these products. The modern methods of preparing animal fats and oils in general, are then exhaustively described.

The various forms of machinery for breaking down the raw material, the pans and apparatus for melting the fat, the presses and filters for separating the oil, are all described in detail with the aid of numerous excellent illustrations, some fifty pages being given to this part of the subject. The methods of preparing the various animal fats and oils are then taken up separately, the processes being described fully, beginning with the raw material and following it through to the finished product.

The properties of the resultant fat or oil are outlined, its uses given, and the adulterants frequently found pointed out.

The various processes of manufacturing the fat products in most common use, are described at length, full details being given of the different stages through which the raw material is taken before the final product is reached. Some thirty pages are devoted to the subject of butter, describing the machinery used in its manufacture, its characteristic properties, and the numerous tests for purity. The manufacture of bone fat, lard, tallow, fish oils, degrass, and wool fat is also fully considered, while numerous other fats and oils but little used are taken up with less detail.

The last pages of the book are devoted to briefly describing the methods used in the examination of fats and oils to determine their purity. The space given to this part of the work is too brief to make it of value to the analyst.

The book is printed on heavy paper with clear type and excellent illustrations. A full table of contents, list of illustrations, and complete index makes it a very satisfactory book for persons interested either theoretically or practically in this subject.

O. S. DOOLITTLE.

**QUANTITATIVE CHEMICAL ANALYSIS BY ELECTROLYSIS.** By DR. ALEXANDER CLASSEN in Cooperation with DR. WALTER LÖB, authorized translation by WILLIAM HALE HERRICK, A.M., and BERTRAM B. BOLTWOOD, PH.D. New York: John Wiley & Sons. xii + 301 pp. Price, \$3.00.

Starting with the dawn of the present century, the science of analysis by electrolysis has made wonderful progress, and within the last twenty years the cumulative data have reached large proportions. The simplicity, cleanliness, and beauty of most of the electrolytic separations, particularly among metals of the sulphide group, have made the subject an especially attractive study to many workers. Among the most indefatigable and revered of these upon the continent, is the chief author of the present work, the sum of whose contributions would make a book in themselves. To the student not familiar with or practiced in electrolytic reactions, this text-book will prove of great assistance, as especial pains have been taken to describe and explain those necessary details that are so often neglected. In

the first or general part of the book, theory alone is considered, the ionic theory of electrolytic dissociation is clearly and concisely given, and the laws governing it are discussed. In the section following are described the various forms of apparatus for the measurement of current magnitudes and tension. The section on current sources is very complete, the best forms of primary and secondary elements being considered in detail, as well as numerous physical methods of producing the current. The section on accumulators is excellent, and the general rules for handling them precise. Numerous examples and tables of experiments are given, to illustrate the working of the apparatus described. The process of analysis under varying conditions is considered in full, and detailed descriptions of special forms of apparatus and the arrangements thereof are outlined. While the simpler arrangements are not slighted, more attention is given to a full description of the equipment of the Electrochemical Institute at Aachen, under the direction of the author. The second general division of the book is devoted to the quantitative determination of the metals, and herein lies the value of the work to the analyst. No criticism of the manner of detailing the various methods can be made, since all the weak as well as the strong points are carefully considered, and the directions are not involved. Full references to all the literature to date are given. Following this the work ends with an appendix of seventy pages containing schematic outlines of some applied examples of electrochemical analysis. Methods for the analysis of brass, bronzes, alloys of different compositions, iron ores, mattes, etc., are given. The work has two indexes, one of authors and one of subjects, and both are complete. The translators have done their work well, and throughout the work make frequent notations from their own experience. The illustrations are all of a high class. As a whole the work is commended either as a text-book or reference book.

W. WALLEY DAVIS.

A MANUAL OF QUANTITATIVE CHEMICAL ANALYSIS. BY E. F. LADD, B.S. New York: John Wiley & Sons. vi + 82 pp. Price \$1.00.

"This little manual is intended for the use of beginners in quantitative analysis \* \* \* ."—*Preface*. For this reason the methods given should be correct if not elaborate. An ex-

amination of the work shows it to contain numerous errors, many of which would get the beginner into serious difficulties. Yet some of the methods were correctly described by the author ten years ago in the Geneva reports.

It is surprising that the reader for any responsible publishing house would recommend the publication of a work containing so many manifest errors.

H. A. HUSTON.

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### ERRATA.

In Vol. 19, p. 886, line 9, "0.30" and "0.22" read "0.030" and "0.022," respectively; and on the same page, line 11, for "0.08" and "0.02" read "0.008" and "0.002", respectively.

In Vol. 20, p. 115, line 34, for "10.2" read "31.8".

In Vol. 20, p. 135, line 13, for "16.4" read "10.4".

In Vol. 20, p. 465, line 5 from bottom, for "from the titration" read "private titration."

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### BOOKS RECEIVED.

Potatoes. Bulletin No. 72. Strawberries. Bulletin No. 73. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Kentucky, 1898.

Variety Tests of Fruits. Bulletin No. 52. Concentrated Feed-Stuffs. Bulletin No. 53. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass. 1898.

Larkspur. Poisoning of Sheep. Bulletin No. 15. Montana Agricultural Experiment Station, Bozeman, Montana, July, 1897.

The Periodical Cicada in West Virginia. Bulletin No. 50. Commercial Fertilizers. Bulletin No. 51. West Virginia Agricultural Experiment Station, Morgantown, West Va., January, 1898.

Memorial of the National Pure Food and Drug Congress to the Congress of the United States. Copies of this pamphlet can be procured from the chairman, Wm. Frear, State College, Pa.

Sugar Beets. Summary of Investigation from 1888 to 1898. Report for 1897. Proposed Experiments for 1898. Bulletin No. 56. April, 1898. Chemical and Agricultural Divisions, Agricultural Experiment Station, Univ. of Minnesota, St. Anthony Park, Ramsey County, Minn.

Twenty-first Annual Report of the Connecticut Agricultural Experiment Station for 1897. Part IV. Experiments on Tobacco. Availability of Fertilizer. Nitrogen. Commercial Fertilizers for Forcing House Crops. Steam Sterilizer for Soils. Composition of Violet Plants and Flowers. Insect Notes. Analyses of Feeds, and of Milk and Butter. Legumin and other Proteids of Legumin. Proteids of Soy Bean. Feed

Tests. Connecticut Agricultural Experiment Station, New Haven, Conn. Red Rice. Bulletin No. 50. Second Series. Agricultural Experiment Station, Baton Rouge, La.

Tenth Annual Report of the Storrs Agricultural Experiment Station, First Part. A Report of the Executive Committee, Treasurer and Director; A Study of the Rations Fed to Milch Cows; Nitrogenous Feeding Stuffs and Formulas for Feeding. Storrs Agricultural Experiment Station, Storrs, Tolland Co., Conn. 128 pp.

Insecticides, Their Preparation and Use. Bulletin No. 126, May, 1898, Connecticut Agricultural Experiment Station, New Haven, Conn. 12 pp.

The Cost of Plant Food in Connecticut, Spring months of 1898. Bulletin No. 127, May, 1898. Connecticut Agricultural Experiment Station, New Haven, Conn. 10 pp.

A Manual of Quantitative Chemical Analysis. By E. F. Ladd, B.S. New York: John Wiley & Sons. 1898. vi + 82 pp. Price, \$1.00.

Bulletin No. 32, Chemical Studies: (1) Drinking Waters; (2) Wool Scouring; (3) Soil Humus; (4) Analysis of Foods; (5) Vinegars. April, 1898. Fargo, N. D.: Government Agricultural Experiment Station for North Dakota. 16 pp.

Jahrbuch der organischen Chemie, unter mitwirkung von B. Rassow, Leipzig; C. Schwalbe, Leipzig; H. Stobbe, Leipzig; J. Troeger, Braunschweig; Herausgegeben von Gaetano Minunui, Palermo. Dritter Jahrgang, 1895. Leipzig: Johann Ambrosius Barth. 1898. x + 1162 pp. Price, M. 30.

A Preliminary Report upon the Bluff and Mississippi Alluvial Lands of Louisiana. By W. W. Clendenin, M.S., M.A. Louisiana State Experiment Station, Baton Rouge, La. 32 pp.

Cattle Tick and Texas Fever. Second Series, No. 51, Bulletin of the Agricultural Experiment Station of Louisiana State University and A. and M. College, Baton Rouge, La. 1898. 54 pp.

Division of Soils. By Milton Whitney. Reprint from the Yearbook of the Department of Agriculture for 1897. 16 pp. Washington, D. C.: Department of Agriculture.

Commercial Fertilizers. By H. A. Huston. Special Bulletin. May, 1898. Purdue University, H. A. Huston, Lafayette, Ind. 8 pp.

Some Interesting Soil Problems. By Milton Whitney. Reprint from Yearbook of Department of Agriculture for 1897. 12 pp.

Nutrition Investigations in Pittsburg, Pa., 1894-1896. By Isabel Bevier, Bulletin No. 52, U. S. Department of Agriculture, Washington, D. C.







